A TEXT BOOK OF FIRE ASSAYING

EDWARD E. BUGBEE

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CHAPTER I.

ASSAY REAGENTS AND FUSION PRODUCTS.

Assaying is a branch of analytical chemistry, generally defined as the quantitative estimation of the metals in ores and furnace products. In the Western part of the United States, the term is employed to include the determination of all the constituents, both metallic and non-metallic, of ores and metallurgical products.

Fire Assaying is the quantitative determination of metals in ores and metallurgical products by means of heat and dry reagents. This involves the separation of the metal from the other constituents of the ore and its weighing in a state of purity.

The reagents used in fire assaying may be classified as fluxes; acid, basic or neutral, and as oxidizing, reducing, sulphurizing or desulphurizing agents. Some reagents have simply one property, as for instance silica, an acid flux, others have several different properties, as litharge, a basic flux but also an oxidizing and desulphurizing agent.

A *flux* is something, which, if added to a body infusible by itself or fusible only with difficulty, will cause it to fuse at a lower temperature than it would have done alone. For instance, quartz by itself is fusible only at a very high temperature, but by adding some sodium carbonate, to the pulverized quartz it can be fused at a temperature easily obtained in the assay furnace.

The student should remember that to aid in the fusion of an acid substance, a basic flux such as litharge, sodium carbonate, limestone, or iron oxide should be added, for a basic substance an acid flux such as silica or borax should be used.

The principal fluxes used in assaying follow:—

Silica, SiO_2, is an acid flux and the strongest one we have. It combines with the metal oxides to form silicates which are the foundation of almost all of our slags. It is used as a flux when the ore is deficient in silica and serves to protect the crucibles and scorifiers from the corrosive action of litharge. Care must be taken to avoid an excess of silica, as too much of it will cause trouble and losses of precious metals by slagging or by the formation of a matte. Silica melts at about 1625° C. to an extremely viscous liquid. (Day & Shepherd). It should be obtained in the pulverized form.

Glass is used by some in place of silica. Ordinary window glass, a silicate of lime and the alkalies with the silica in excess, is best. Its acid excess is always doubtful and so is not commonly used. If used, a blank assay should be run on each new lot to insure against introducing precious metals into the assay in this way. Its chief advantage is that 5 or 10 grams too much glass will ordinarily do no harm in a fusion whereas 5 or 10 grams of silica in excess might spoil it.

Borax, $Na_2B_4O_7,10H_2O$, acts as an acid flux. It contains a large amount (47 per cent) of water which is given off on heating. During the heating, the borax swells to more than twice its original bulk, and if an excess of it is used, and especially if not thoroughly mixed with the charge, it may force part of the charge out of the crucible. It should never be used for scorification work.

Borax Glass, $Na_2B_4O_7$, is an active, readily fusible, acid flux. It is made by fusing borax in a crucible and pouring the fused mass on a clean iron or brick surface. It should be crushed to pass a 16 or 20 mesh screen before using. Crystaline borax glass melts at 742° C. Finely divided amorphous borax glass begins to sinter at 490°–500° C. It is extremely viscous when melted.

Its rational formula $Na_2O, 2B_2O_3$ indicates an excess of acid and experiment proves this to be the case. It is an excellent flux for all the metallic oxides, and fusing as it does at a low temperature, it helps to facilitate the slagging of the ore. Either borax or borax glass is used in almost every flux mixture. It should be used in preference to silica as a flux for lime, magnesia, iron, manganese and zinc oxides.

Borax glass cannot always be used in preference to borax, as it is more violent in its action and causes much boiling of the charge. The fine material especially takes on moisture from the air and tends to cake. It is sometimes used as a cover on top of a crucible charge, especially in muffle fusions. Here it melts before the rest of the charge and prevents loss of the fine ore by "dusting."

Sodium bicarbonate, $NaHCO_3$, is the most common of the alkali carbonate fluxes. It is decomposed on heating to 276° C. forming the normal carbonate as shown by the following reaction:—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

It acts as a basic flux, a desulphurizing agent and in some cases as an oxidizing agent. It is the cheapest of the alkali carbonates, and, as it is readily obtained pure, and does not deliquesce, it is preferred by many to the normal carbonate.

Sodium carbonate, Na_2CO_3, (normal carbonate) melts at 852° C. It occurs crystallized, (sal-soda) containing more than half its weight of water, and in this form, is not at all suited for a flux. In the anhydrous form, it is somewhat stronger, weight for weight, than the bicarbonate, but unfortunately it tends to absorb water from the air and is therefore unsatisfactory for use in some climates. The commercial normal carbonate of this country is made by the Solvay process from the bicarbonate and should be very pure. The variety known by the trade as, 58% dense, soda-ash has been found entirely satisfactory for assay purposes and is but little affected by atmospheric moisture.

It acts as a basic flux, a desulphurizing agent, and in some cases, an oxidizing agent. Heated in the presence of silica, it breaks up giving off CO_2 and the Na_2O combines with the silica forming silicates, as for example:—

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

Many of these silicates are readily fusible and for this reason soda is used in nearly every fusion.

Potassium carbonate, K_2CO_3, fused at 894° C. and is also a basic flux. Its action is in all ways similar to sodium carbonate.

A mixture of sodium and potassium carbonates fuses at a lower temperature than either one alone, due to the formation of a double salt and therefore the mixture is used whenever it is desired to maintain a low temperature during the assay. The lead assay is a case in point.

Potassium carbonate should be kept in an air tight receptacle as otherwise it takes on water from the air and forms a hard cake.

Litharge, PbO, (92.83% lead) is a readily fusible basic flux. It acts also as an oxidizing and desulphurizing agent and on being reduced it supplies the lead necessary for the collection of the gold and silver. It melts at 883° C. (Mostowitsch).

Litharge begins to combine with silica at 600° C. forming lead silicates which are pasty at this temperature.

$2PbO + SiO_2 = Pb_2SiO_4$ (monosilicate). This silicate is fusible at a low temperature 746° C. and is as fluid as water. If the proportion of silica be raised above that of the tri-silicate, the mixture becomes less easily fusible and is decidedly viscous when fused. Litharge has such a strong affinity for silica that if enough is not supplied to it in the crucible charge, it will attack the acid material of the crucible itself and if left long enough will eat a hole through it.

Litharge readily gives up its oxygen if heated with carbon, carbonic oxide, hydrogen, sulphur, metallic sulphides, iron, etc. The reaction with carbon begins at about 550° C. It thus acts as an oxidizing, and in the presence of sulphur, as a desulphurizing agent:—

$2PbO + C = CO_2 + 2Pb$ (oxidizing)

$3PbO + ZnS = ZnO + SO_2 + 3Pb$ (desulphurizing and oxidizing)

The liberated lead is then available for the collection of the gold and silver.

Lead silicates do not readily give up their lead to carbonaceous and sulphurous reducing agents. The higher the proportion of silica, the less readily is the silicate broken up. In order to extract all the lead it must first be set free by the use of a stronger basic flux. Thus "metallic iron decomposes all fusible lead silicates at a bright red heat, provided enough is added to form a singulo-silicate." (Hofman).

Ordinary commercial litharge contains a small amount of silver, varying from 0.2 oz. to 1.0 oz. or over per ton. A practically silver free variety is made from Missouri lead by giving a zinc treatment, as for the Parkes process and then cupelling. It is never safe to assume, however, that litharge is silver free until it has been proven so by assay. Each new lot received should therefore be carefully mixed to make it uniform and assayed. See page 89.

Lead in the granulated form (test lead) is used in the scorification assay as a collector of the precious metals and as a flux. When oxidized by the air of the muffle it becomes a basic flux. Ordinary test lead usually contains more or less silver and every new lot should be assayed before being used. Lead melts at 326° C.

Test lead may be made by pouring molten lead just above its freezing point into a wooden box and shaking it violently in a horizontal direction just as it becomes pasty and continuing until it becomes solid. The fine material is sifted out, the coarse is re-melted.

Argols is a reducing agent and basic flux. It is a crude bitartrate of potassium obtained from wine barrels. It is one of the best reducing agents.

Cream of tartar, $KHC_4H_4O_6$, is refined bitartrate of potassium. Being free from sulphur it is used as a reducing agent in the copper assay. Both argols and cream of tartar break up on heating as follows:—

$$2KHC_4H_4O_6 + \text{heat} = K_2O + 5H_2O + 6CO + 2C$$

The K_2O thus liberated being available as a flux.

Charcoal, sugar, flour etc. are also reducing agents because of the carbon that they contain. Flour is very commonly used in flux mixtures and is satisfactory in every respect.

Sulphides, arsenides, antimonides etc. in ores all have a reducing effect.

To determine the reducing power of the different minerals and reducing agents see chapter on the crucible assay.

Iron is a desulphurizing and reducing agent. When heated with the sulphides of lead, silver, mercury, bismuth and antimony the sulphides are decomposed yielding a more or less pure metal and iron sulphide. Copper, nickel and cobalt sulphides are partly reduced by iron as would be expected by a study of the heat of formation of the same.

It also reduces most of these metals and some others from their oxide combinations, as for example:—

$$PbO + Fe = Pb + FeO$$

The iron oxide formed acts as a basic flux. Iron decomposes all fusible lead silicates by replacing the lead, thus:—

$$2PbO.SiO_2 + 2Fe = 2FeO.SiO_2 + 2Pb$$

It should therefore always be used in the lead assay.

It is used in the form of spikes or nails and sometimes, especially in Europe, an iron crucible is employed.

Potassium nitrate, KNO_3, commonly known as niter is a powerful oxidizing agent and also a basic flux. It melts at 339° C. and fuses without alteration at a low temperature, but at a higher temperature breaks up giving off oxygen which oxidizes sulphur and many of the metals, notably lead and copper.

It is used in the fire assay especially to oxidize sulphides, arsenides, antimonides, etc.

In a charge containing a large excess of soda and litharge the reaction with pyrite is as follows:—

$$6KNO_3 + 2FeS_2 + 3Na_2CO_3 = Fe_2O_3 + 3K_2SO_4 + 3Na_2SO_4 + 3CO_2 + 3N_2$$

In this case one gram of niter would oxidize 0.39 grams of pyrite, or its oxidizing power would be 4.75 taking the reducing power of pyrite in this type of charge as 12.20.

In a charge containing considerable silica the reaction with pyrite is about as follows:—

$$10KNO_3 + 4FeS_2 + 2SiO_2 = 2Fe_2SiO_4 + 5K_2SO_4 + 3SO_2 + 5N_2$$

In this case one gram of niter would oxidize 0.475 grams of pyrite. Taking the reducing power of pyrite as 9 in this type of charge, the oxidizing power of niter in terms of lead is 4.27. This latter is more nearly the figure obtained in practice. As a little oxygen usually escapes unused and as the commercial article is never absolutely pure, a figure as low as 4.0 is often found about right for practice.

Niter also reacts with carbon and silica as follows:—

$$4KNO_3 + 5C = 2K_2O + 5CO_2 + 2N_2$$

or 1 gram of niter oxidizes 0.15 grams of carbon,

$$2KNO_3 + SiO_2 = K_2SiO_3 + 5O + N_2$$

This action begins at about 450° C.

If finely divided lead is fused with niter, the lead is found to be directly oxidized by the niter. Fulton found the oxidizing power of niter used in this way to be 2.37. The following reaction shows approximately what happens:—

$$7Pb + 6KNO_3 = 7PbO + 3K_2O + 3N_2 + 4O_2$$

It should be noted that in this case a considerable portion of the oxygen escapes unused.

Many assayers object to the use of niter because of its oxidizing effect on silver. Large amounts of niter cause violent boiling of the crucible charge and necessitate careful heating to prevent loss. It is found to give less trouble when the crucible is uniformly heated, as in the muffle, than when the charge begins to melt first at the bottom, as in the pot furnace. The student should select an extra large crucible and carefully watch the fusion when using more than 20 or 30 grams of niter in any charge.

Potassium cyanide, KCN, is a powerful reducing and desulphurizing agent. It combines with oxygen forming potassium cyanate, thus:—

$$PbO + KCN = Pb + KCNO \quad \text{(reducing action)}$$

and also with sulphur, forming sulphocyanide, as follows:—

$$PbS + KCN = Pb + KSCN$$

It is sometimes used in the lead assay and usually in the tin and bismuth assays. It is extremely poisonous, and should be handled with great care. It fuses at 526° C.

Salt, (sodium chloride) NaCl, melts at 819° C. and is used as a cover to exclude the air, and to wash the sides of the crucible, and prevent small particles of lead from adhering thereto.

It does not enter the slag, but floats on the top of it. It is often colored by the different metallic oxides of the charge and sometimes helps to distinguish assays which have become mixed in pouring.

Fluorspar, CaF_2, is occasionally used as a flux. It fuses at a high temperature, 1400° C., but when melted, it is very fluid and assists in liquifying the charge.

Cryolite, $AlNa_3F_6$, is not commonly used by assayers, but it is sometimes used in melting bullion. It fuses at a low temperature, and has the property of dissolving alumina.

TABLE 1. ASSAY REAGENTS.

Name	Formula	Properties in order of their importance.
Silica	SiO_2	Acid flux
Glass	$xNa_2O.yCaO.zSiO_2$	Acid flux
Borax	$Na_2B_4O_7.10H_2O$	Acid flux
Borax glass	$Na_2B_4O_7$	Acid flux
Sodium bicarbonate	$NaHCO_3$	Basic flux, desulphurizing
Sodium carbonate	Na_2CO_3	Basic flux, desulphurizing
Potassium carbonate	K_2CO_3	Basic flux, desulphurizing
Litharge	PbO	Basic flux, desulphurizing, oxidizing
Potassium nitrate	KNO_3	Oxidizing, desulphurizing
Argols	$KHC_4H_4O_6 + C$	Reducing agent, basic flux
Cream or tartar	$KHC_4H_4O_6$	Reducing agent, basic flux
Flour		Reducing agent
Charcoal	C	Reducing agent
Lead	Pb	Collecting agent
Iron	Fe	Desulphurizing and reducing agent
Potassium cyanide	KCN	Reducing and desulphurizing agent
Salt	$NaCl$	Cover and wash
Fluorspar	CaF_2	Neutral flux
Cryolite	$AlNa_3F_6$	Neutral flux

Fusion Products.

Every gold, silver or lead assay fusion, if the charge is properly proportioned and manipulated, should show two products, a lead button and above it a slag. Two undesirable products, matte and speiss are occasionally also obtained.

The lead button should be bright, soft and malleable and should separate easily from the slag.

The slag is usually a silicate or borate of the metallic oxides of the ore and fluxes used. It should be homogeneous and free from particles of undecomposed ore. A good slag should usually be more or less glassy and brittle. When poured, the slag should be thin and fluid and free from shots of lead. If too acid, it will be quite viscous and stringy, and the last drops will form a thread in pouring. If too basic, it will be lumpy and break off short in pouring. When cold, the neutral or acid slag is glassy and brittle, the basic one is dull and stony looking.

The slags should never be allowed to get mixed with the fuel, as they quickly destroy the furnace lining.

Matte, is an artificial sulphide of one or more of the metals, formed in the dry way. In assaying it is most often encountered in the niter fusion of sulphide ores when the charge is too acid. It is found lying just above the lead button. It is usually blue gray in color, approaching galena in composition and is very brittle. It may be in a layer of considerable thickness, or may appear simply as a granular coating on the upper surface of the lead button. This matte always carries some of the gold and silver and as it is brittle, it is usually broken off and lost in the slag, in the cleaning of the lead button. The student should examine the lead button as soon as it is broken from the slag, and if any matte is found, he may be certain that his charge or furnace manipulations are wrong.

Speiss, is an artificial, metallic arsenide or antimonide formed in smelting operations. As obtained in the fire assay, it is usually an arsenide of iron approaching the composition of Fe_5As. Occasionally the iron may be replaced by nickel or cobalt. The antimony speiss is very rare. In assaying, speiss is obtained when the iron method is used on ores containing arsenic. It is a hard, fairly tough, tin white substance found directly on top of the lead and usually adhering tenaciously to it.

If only a small amount of arsenic is present in the ore, the speiss will appear as a little button lying on top of the lead, if much arsenic is present, the speiss will form a layer entirely covering the lead. It carries some gold and silver. If only a gram or so in weight, it may be put into the cupel with the lead and will be oxidized there, giving up its precious metal values to the lead bath. A large amount of speiss is very hard to deal with as it is difficult to scorify. The best way is to repeat the assay using some other method.

CHAPTER II.

FURNACES AND ASSAY SUPPLIES.

Furnaces for assaying may be divided into the two following classes:—

1. **Crucible or Pot-Furnaces.** These are furnaces used solely for melting purposes in which the crucible is in direct contact with the fuel or flame and the contents therefore more or less subject to the action of the products of combustion.

2. **Muffle-Furnaces.** These are furnaces in which the charge to be heated is in a space (the muffle) apart from the fuel or products of combustion. The muffle is a semi-cylindrical receptacle of fire-clay or other refractory material set horizontally and so arranged that the fuel or products of combustion pass around and under it. Thus the material to be heated is entirely separated from the products of combustion.

As muffle furnaces may be used for melting purposes as well as for scorification and cupellation, many assayers in America use this type of furnace exclusively, especially in connection with soft-coal fuel. The advantages of muffle furnaces for melting are the greater ease and saving of time in charging and pouring, the better control of temperature and the better distribution of heat for melting purposes. Crucibles also seem to stand more heats in a muffle furnace than they will in pot furnaces, due no doubt to the slower and more uniform heating.

Pot-furnaces have the advantage of size, so that for instance in dealing with low-grade ores a larger charge and crucible may be used than in the ordinary size muffle furnaces. A higher temperature may be obtained in pot-furnaces than in muffles and this occasionally is an advantage of the pot-furnace.

The furnaces themselves are made of fire-brick or fire-clay tile and may be set in an iron jacket or surrounded by common red brick. Fire-brick is best laid in a mortar made from a mixture of two parts ground fire-brick and one part fire-clay. Sometimes a small amount of Portland cement is added. In any event the brick and tiles should be thoroughly wet previous to applying the mortar. Finally, as little mortar as possible should be used since the bricks are much harder than the solidified mortar.

Assay furnaces are made to burn practically all kinds of gaseous, liquid and solid fuels. Those most commonly used are natural and artificial gas, gasoline, kerosene, crude-oil, wood, charcoal, coke, bituminous and anthracite coal.

Gas is the cleanest, most easily controlled, most efficient in combustion and except in the case of a natural supply the most expensive fuel. A blower is usually required to supply air under a low pressure with this method of firing.

Oil is nearly as clean and as convenient to use as gas, the efficiency of combustion is high and in localities near the oil-fields it may be very cheaply obtained. The calorific power of the hydro-carbon fuel oils is high, about 50% more than the best coals, which makes them particularly suited for use in isolated localities where freight charges are high. Gasoline is forced under pressure through a heated burner where it is vaporized and the gas injected into the furnace carries with it a sufficient supply of air for combustion. Crude-oil requires steam or air under pressure to aid in atomizing the oil preliminary to proper combustion. Gasoline, kerosene and crude petroleum all have a heating value of about 21,000 B.T.U. per pound.

Solid fuels are usually the cheapest and are therefore more extensively used than any of the others. In isolated districts where coal or coke is not available wood is occasionally used as fuel in assay furnaces. For this purpose it should be felled in winter and thoroughly air dried for at least six months or longer according to the climate. The air-dried wood will still retain from 20 to 25 per cent of water and in this condition has a heating value of about 6000 B.T.U. per pound. Charcoal is seldom used in this country for assay purposes on account of the abundant supply of other fuels.

Bituminous-coal is the most satisfactory solid fuel for muffle furnace firing and coke for pot furnaces. Good soft-coal has a calorific power of about 14,500 B.T.U. per pound, should be low in sulphur and the ash must not be too readily fusible. Coke should be hard and strong, low in sulphur and the ash should be infusible at the temperature of the furnace. That is to say it should be high in silica and alumina and low in iron, calcium, magnesium and the alkalies to prevent clinkering of the walls of the furnace.

Gas and Oil vs. Solid Fuel. Gaseous and liquid fuels have many advantages over solid fuels for assay purposes, some of which are as follows:—

1. The fire is kindled in an instant and the furnace may be quickly heated to the desired temperature for work.
2. The temperature is readily controlled and may be quickly varied to suit the requirements of the work.
3. A high efficiency of combustion is possible in properly designed furnaces and as soon as the work is completed the fuel supply may be shut off and fuel consumption stopped.
4. The avoidance of labor in firing gives the assayer more time for other duties.
5. The cleanliness in operation due to absence of solid fuel and ash is obviously a great advantage in any analytical laboratory.

On account of the expense however coal is much more generally used than either oil or gas. It is easy to make a comparison of the costs of any of the fuels by considering the heat units. For instance, with soft-coal at $5.00 per ton and gasoline at 15c per gallon we may say that one cent invested in soft-coal will buy us $4 \times 14{,}500 = 58{,}000$ B.T.U. and that the same amount invested in gasoline will bring approximately $\frac{1}{15} \times 5.4 \times 21{,}000 = 7560$ B.T.U. That is to say the gasoline is over seven times as expensive as the coal on the basis of heat units and for steady running this may be taken to be approximately correct. However for a small amount of work a gasoline furnace may be cheaper to run even with the cost of fuel as above assumed, for the small furnace is quickly heated and as soon as the work is completed the oil supply may be shut off and the expense stopped, while a coal furnace takes much longer to heat and then must be allowed to burn out after the work is completed.

Coal Furnaces. This type of furnace is used in most of the large custom and smelter assay offices in this country.

The furnace may be built either with a tile or fire-brick lining. The tile lining is more easily set up but whether or not it is as durable as a properly constructed fire-brick lining is open to question. The outside of the furnace is usually laid up with common hard-burned red brick. If the furnace is to be lined with fire-brick several rows of headers should be left to hold the lining securely in place. The furnace is held together with angle-irons, stays and tie-rods.

In the furnace as ordinarily constructed the muffles are supported by "jamb" bricks projecting from the sides. When these are used it is well to leave a hole or lose brick on the outside of the furnace to facilitate removing the stubs when these bricks become broken off and the ends slagged in. Fulton recommends using long tiles here which meet in the center, thus giving better support for the muffle. He claims a prolonged life for the muffle with this arrangement. The writer has found the Scotch Gartcraig brick to outlast 3 or 4 best American fire-brick for muffle supports. Another method of supporting muffles in furnaces of this type is by the use of iron pipes or castings extending directly across the furnace and through which cooling water is circluated.

These furnaces occupy a floor space of approximately three and one-half by four feet. They are built in a variety of sizes, those taking NN, QQ and UU muffles are the sizes most commonly used. The NN muffle is $10\frac{1}{2} \times 19 \times 6\frac{1}{2}$ inches outside, similarly the QQ is $12\frac{1}{2} \times 19 \times 7\frac{3}{4}$ and the UU is $14 \times 19 \times 7\frac{1}{4}$ inches outside.

Each NN muffle will hold twelve–20 gram or eight–30 gram crucibles allowing in each case for a row of empty crucibles in front to act as warmers, while the QQ muffle will hold fifteen–20 gram or twelve–30 gram crucibles also allowing for a row of empty crucibles in front.

The furnaces are best arranged to be fired from the rear although they may be arranged to be fired from the front or sides. The flue makes off from near the front of the furnace thus tending to heat the muffle uniformly throughout its entire length. It should be from one-sixth to one-eighth the grate area.

The stack for one of the furnaces will need to be at least 20 feet high and possibly higher depending largely on the character of the coal. It should not be built directly on the furnace but may be placed directly over the furnace if supported by arches and cast-iron columns, or it may be put to one side of the furnace and in this case will extend down to the ground. When the stack is supported independently of the furnace it allows the furnace to expand and contract with less danger of cracking and also permits of tearing down and rebuilding the furnace without interfering with the stack.

With long-flame coal these furnaces are best fired with a rather thin bed of fuel say 8 inches. The sequence of firing will consist of first running the slice bar along the entire length of the grate in one or two places and lifting up the fire to break up any large cakes and thus allow free passage of air through the fire, second to push the well coked coal forward with the hoe and third to add 2 or 3 shovels of fresh coal near the firing door. As this coal is heated it begins to coke and the gas given off passes over the white-hot coal of the fire and is there mixed with heated air. This results in a free draft and good volume of hot flame. If instead of adding the fresh coal near the firing door it is spread all over the fire it will quickly cake and tend to smother the fire by shutting off the draft.

The temperature of the muffle may be regulated at will by manipulating the draft and firing doors. For instance, after a batch of cupels have started the draft may be closed and the firing door opened thus admitting cold air above the fire which quickly cools the muffles to any required degree.

Wood Furnaces. Wood-burning furnaces are made with single and double-muffles and are much like the soft-coal furnaces except that a larger fire-box and grate are used. Wood is usually sawed in half-cord lengths and with dry wood the muffle may be easily heated sufficiently for assaying. Hard wood is much to be preferred as it does not burn out as rapidly, but almost any kind of dry wood may be used.

The large fire-box and the grate which is set about 8 inches below the bottom of the fire-door are the principal distinguishing characteristics of a wood burning assay furnace.

Coke Furnaces. Coke is still used to a considerable extent in pot furnaces but for muffle furnace fuel it is fast falling into disuse, at least in this country.

Comparing the coke and the soft-coal muffle furnace the coke furnace has the advantage that it can be more quickly heated to a cupelling temperature and that it requires less frequent stoking. On the other hand it is harder to regulate the temperature, especially to cool it off quickly when cupelling, the stoking is harder work and the fuel cost per assay is higher in most localities.

The great advantage of the coke pot-furnace is the very high temperature which may be obtained and the fact that even though the crucibles boil over or eat through no harm is done to the furnace. Coke furnaces especially should be supplied with a good quality of fuel. If the ash tends to melt the walls become quickly covered with clinkers and are bound to be more or less damaged when these are removed.

Gasoline Furnaces. A gasoline furnace outfit consists of a furnace which may be either a muffle, crucible or combination of the two, a burner with piping etc. and a gasoline tank with pump. The latter for a small assay office consists of an ordinary tinned-steel pressure tank equipped with a hand pump, pressure-gauge and the necessary piping connections. These range from 2 to 15 gallon capacity.

The burners are usually constructed of special bronze alloys capable of withstanding oxidation at high temperatures. They consist of a filtering chamber for purifying the gasoline, a generating chamber where the gasoline is vaporized, a generating pan and valve for the initial heating of the burner, a spraying nozzle and valve through which the gasoline vapor is injected into the furnace and a mixing chamber where the proper amount of air for combustion is mixed with the gas. From the filter the gasoline passes around the interior of the burner face (the generating chamber), where it is heated by the radiated heat from the furnace and vaporized so that once the furnace is under way the generating burner may be shut off. Gasoline is supplied to the burner under a pressure of from 20 to 50 pounds per square inch.

The great feature to be sought and one of the hardest to attain in any gasoline furnace is an even distribution of heat. Another feature found wanting in many gas and gasoline furnaces is the poor draft through the muffle. Owing to the fact that the pressure inside the furnace is slightly greater than the outside pressure there is a great tendency for the products of combustion to work back through the hole in the rear of the muffle, thus to a large extent excluding the air and unduly prolonging cupellation or scorification.

In operating a gasoline burner care should be taken to see that combustion takes place only in the furnace. All burners have more or less tendency to back-fire, that is for the flame to jump back and continue in the mixing chamber. If this is allowed to continue the burner gets so hot that the metal oxidizes and then it is only a matter of a short time before it is entirely destroyed. Every furnace should be provided with a shut-off valve between the burner and the gasoline tank. When it is desired to shut off the furnace, close this shut-off valve letting the burner continue as long as any pressure is left and do not ever entirely close the burner valves. The valve stem or needle is of steel and the seat is of bronze and owing to the different rates of expansion of these metals the valve is injured if these are left in close contact when the burner is cooling. This precaution is especially to be observed when the burner is provided with the ordinary needle valve, as when this valve is once enlarged the whole efficiency of the burner is destroyed.

Gas Furnaces. Gas furnaces are used in some assay offices, especially where a natural gas supply is available. Where artificial gas has to be used this type of furnace proves decidedly expensive if used for any considerable amount of work. As the gas is usually not under sufficient pressure to carry in its own supply of air for combustion, these furnaces are customarily supplied with air from a blower, which adds to the expense and difficulty of the furnace operation.

Crude Oil Furnaces. When a cheap oil supply is available crude oil is frequently used as an assay fuel. The furnaces themselves are built exactly as for gasoline firing.

Crude-oil and kerosene cannot be vaporized in the burner as they deposit carbon when heated and thus clog the tubes. Consequently to insure complete combustion the oil must be thrown into the furnace in as fine a state of mechanical subdivision as possible. This is accomplished by atomizing the oil with a jet of steam or air. The steam may be from an outside source or may be generated in the face of the burner from the heat reflected from the furnace. The Marvel burner made by the Braun Corporation of Los Angeles uses the latter method of supplying steam. This burner requires to be heated by a torch or alcohol lamp to start and the necessary outfit includes two pressure tanks one for oil and one for water. Oil of any gravity up to 60°, Beaume may be used with this burner.

Furnace Repairs.

Fire-clay usually forms the basis of mortars used in furnace construction and repairs, as lime mortar and hydraulic cement are not suited for use with masonary exposed to high temperatures. Fire-clay is a clay containing only very small amounts of iron, lime, magnesia and the alkali oxides. It forms a more or less plastic and sticky mortar and on heating loses its moisture and plasticity and the mortar hardens.

All clays shrink more or less on drying and burning and to prevent this as far as possible in the mortar as well as to make it strong a certain amount of crushed fire-brick or sand should be added. Crushed fire-brick is better than sand owing to its porous and irregular shaped grains as these give a better mixture with the clay and a stronger cement.

A good mortar for general use around assay furnaces is made with a mixture of two parts ground fire-brick through 12 mesh and one part fire-clay. A small amount of Portland cement or molding clay, say not over one-third part, will make the mixture adhere better and the mortar will be harder when set. For work at very high temperatures the Portland cement must be omitted as it acts as a flux for the other materials and causes the whole to melt.

All mortars should be made up dry and thoroughly mixed before the required amount of water is added. The water should be thoroughly mixed in and the mortar should be sticky and of the right consistency. It is well to mix the mortar several hours before using. When laying bricks or making repairs about a furnace the bricks and brick work should be thoroughly wet before applying the mortar as otherwise the bricks absorb so much water that the mortar does not form a good bond with them.

In laying fire-bricks as little mortar as possible should be used as the bricks are always harder than even the best of mortar. The mortar should be made to fill every crevice. The best way to attain this is to put an extra amount of fairly thin mortar on the wet brick and then drive or force it firmly into place, allowing the excess mortar to squeeze out.

The ash from many coals is quite readily fusible and results in the formation of clinkers and accretions on the sides of the furnace, especially just above the grate. When the furnace is cold these adhere very tenaciously to the walls of the furnace and in breaking them off, pieces of the brick are removed with them. To remove these accretions with the least damage to the furnace they should be cut off with a chisel bar just after a hot fire has been drawn.

In putting in a new muffle, first remove the old one with the mortar that held it, also any clinkers which would interfere with the working of the furnace. Patch the lining of the furnace if it requires it and see that the bricks or other supports for the muffle are in place and in good condition. After trying the muffle to see that it rests properly on the supports, remove it, sponge over the brick work where the mortar is to come in contact with it, place some rather thick mortar on each of the supports and replace the muffle. See that it rests evenly on the different supports and on the front wall of the furnace. The muffle should be level horizontally and slope slightly toward the front end. Fill up the space between the muffle and the front wall of the furnace with some rather thick mortar, working from both inside and outside of the furnace. This outside joint should be finished up neatly with the aid of a trowel. It is best to allow the furnace to dry for a day or two if possible, but if necessary it may be used as soon as finished by heating up slowly.

For patching the linings of furnaces use the mixture recommended for general use or try the following which is recommended by Lodge. Fire-brick through 12 mesh 7 parts, Portland cement 2 parts, fire-clay 1 part. Put this on as dry as possible and it will make a patch almost as hard as the original brick.

Cracked and broken muffles may be made to last much longer if patched with some of the following mixtures.

When the bottom is almost gone Lodge recommends a mixture of 2 parts Portland cement, 1 part ground fire-brick, $\frac{1}{3}$ to $\frac{1}{2}$ part fire-clay. For patching holes he recommends a mixture of glass, sand and clay to which a little litharge has been added. After heating this becomes as hard as the muffle. A mixture of short fibered asbestos and silicate of soda is also recommended.

Metallurgical Clay Goods.

Under the caption metallurgical clay goods are included muffles, crucibles, scorifiers, roasting dishes, annealing cups etc. These embrace many of the most important utensils of the assayer and upon their good properties much of his success depends. Fire-clay is the only material which answers the double purpose of satisfactory service and inexpensive construction. Refractory clay or fire-clay as it is commonly called is a clay which will stand exposure to a high temperature without melting or becoming in a sensible degree soft or plastic.

All clays contract both upon drying and burning and this leads to more or less warping and cracking of the finished product. To prevent this shrinkage as far as possible and also to add strength to the finished article it is customary to add a certain amount of sand or well burned clay to the mixture. Burned clay is usually preferred to sand for this purpose, not only because its rough porous grains give a better bond with the fire-clay and make a stronger cement, but it also makes an article which is less readily corroded by assay slags and fusion products. The intermixture of coarse grains of burned clay helps also in that it makes a product better able to withstand sudden changes in temperature.

The exact proportions of raw and burned clay used by any manufacturer are carefully guarded trade secrets and depend of course very much on the clay used as well as upon the article to be manufactured. The larger the article the more is the care which must be taken to prevent warping and cracking. Usually however, the proportion of raw to burned clay will lie between the limits of one to one and one to two.

Muffles. Muffles may be made of a variety of materials but for assay purposes fire-clay muffles are used exclusively. They are made in a great variety of sizes and shapes.

Muffles as well as other fire-clay ware should be stored in a warm, dry place and should be heated and cooled slowly and uniformly for maximum service. The life of a muffle is also much influenced by the manner of supporting.

Crucibles. Assay crucibles are made either of a mixture of raw and burned clay or of a mixture of sand and clay, the first being known as clay or fluxing crucibles and the second as sand crucibles. The raw clay is finely ground, mixed with the right proportion of coarser particles of sand or burned clay and water and the whole well kneaded and compressed in molds of the proper shape.

Good crucibles should have the following properties:—

1. Ability to withstand a high temperature without softening.
2. Strength to stand handling and shipping without breaking.
3. Ability to stand sudden changes of temperature without cracking.
4. Ability to withstand the chemical action of the substances fused in them.
5. Impermeability to the substances fused in them and to the products of combustion.

Of course it is impossible to get any one crucible which will possess all of the above good properties to a high degree. For instance if a crucible is to be made as nearly impermeable as possible it will be made of very fine grained material and tightly compressed. Such a crucible however will not stand handling or sudden changes of temperature as well as one made with a skeleton of coarser material. Furthermore the manner and temperature of burning has much to do with the way that crucibles will stand handling and shipping. A fairly hard burned crucible will be stronger and less likely to be broken in handling but on the other hand it will not stand sudden changes of temperature as well as a soft-burned crucible. Crucibles made of clay containing little uncombined silica and of burned clay of the same nature will stand a high temperature and chemical corrosion much better than those made of sand and clay or of clay containing much free silica.

Crucibles are tested for resistance to chemical corrosion by actual service and also by fusing litharge in them and noting the time it takes to eat through. To make a test of this sort which is of any value care must be taken to see that the temperature, the quantity of litharge and all other conditions are the same for the crucibles being tested. A crucible may be tested for its permeability to liquids by filling it with water and noting the time it takes before it becomes moist on the outside.

Crucibles come in a great variety of shapes and sizes. Those most commonly used for assaying may be classified into two groups as follows:—

Pot Furnace Crucibles. These are comparatively slim, heavy walled crucibles with practically no limit as to height. The base is small so that they may be forced down into the fuel and for this reason they are easily tipped over and are not suitable for muffle work. The sizes most used are the E, F, G, H, J and K. Crucibles of the same designation made by different manufacturers vary considerably in capacity. The approximate capacity of some of the pot-furnace crucibles is shown in the following table:—

TABLE II. CAPACITIES OF POT FURNACE CRUCIBLES.

Crucible designation	E	F	G	H	I	J	K
[1] Battersea	180cc	210cc	300cc	420cc	–	600cc	750cc
[2] Denver	180cc	240cc	400cc	–	530cc	685cc	950cc

[1] Made by the Morgan Crucible Co. London, England.
[2] Made by the Denver Fire Clay Co. Denver, Colorado.

Muffle Crucibles. These are made with a broader base so that they may stand securely on the floor of the muffle and are usually not more than four inches high. Muffle crucibles are designated by gram capacity, the 10, 15, 20 and 30 gram sizes being most frequently used. The intention of the system is that the numbers indicated the grams of ore charge which the crucibles will take. They are usually generously proportioned so that often an assay ton of ore (29.166 grams) may be treated in a 20 gram crucible.
The approximate capacity of the more important muffle crucibles is shown in the following table:—

TABLE III. CAPACITY OF MUFFLE FURNACE CRUCIBLES.

Crucible Designation	5 gm.	10 gm.	12 gm.	15 gm.	20 gm.	30 gm.
Denver	70cc	100cc	140cc	160cc	190cc	260cc
Battersea	70cc.	100cc	–	135cc	190cc	260cc

Scorifiers. These are shallow fire-clay dishes used in the scorification assay of gold and silver ores. They should be smooth on the inside, dense and impermeable to lead and slag and should be composed so as to withstand as much as possible the corrosive action of litharge. Scorifiers are designated by their outside diameters. Of the large number of sizes made the following are the most commonly used: $2\frac{1}{4}''$, $2\frac{1}{2}''$, $2\frac{3}{4}''$, $3''$, $3\frac{1}{2}''$. The Bartlett scorifier is shallower than the regular one and was designed for the treatment of heavy sulphide ores containing considerable metallic impurities. Scorifiers particularly should be made of clay containing a minimum of uncombined silica, as the scorifier slags are usually very basic. Particularly when they contain copper they attack the silica of a scorifier with avidity and one with a siliceous skeleton may become perforated and allow its contents to escape onto the floor of the muffle, thus spoiling the assay and injuring the muffle.

CHAPTER III.

SAMPLING.

Definition. A sample is a small amount which contains all the components in the same proportions as they occur in the original lot.

The object of sampling an ore is to obtain for chemical or mechanical tests a small amount which shall contain all the minerals in the same proportion as they occur in the original lot. In the subsequent discussion the word "sample" will be taken to mean that fraction which is taken to represent the whole, whether or not it does so. The compound words correct-sample, representative-sample, true-sample, will be used to represent the ideal conditions.

In the intelligent operation of a mine or metallurgical plant, it is necessary to sample and assay continually. In most mines, the different faces of ore are sampled every week, sometimes every day. In concentrating plants, it is customary to sample the products of every machine to ascertain whether the machine is doing the work expected of it. In smelters, every lot of ore, as well as fluxes and fuels, have to be sampled and assayed in order to calculate a charge which will run properly in the furnace. The slag, flue dust and metallic products must also be sampled and assayed in order to maintain control of the operations. In lixiviation plants, the ore and tailings as well as the solutions must be sampled in order to control and check the daily work of the plant. In fact, careful sampling and assaying can not be disregarded, and is becoming more and more important every day as the grade of ore decreases and the margin of profit becomes less.

The assayer will usually have the major part of the sampling done for him, but he is expected to know how to do it when called upon. He will usually have only to prepare the final sample, but will occasionally receive lots of 10 to 100 or more pounds to assay in which case he will have do to his own sampling. The following discussion will deal principally with the assay laboratory problems of sampling and the questions of mine and mill methods will be omitted.

Labelling Samples. Every lot of ore coming into an assay office, laboratory, custom mill or smelter should be given a lot number which should never be repeated, and should be immediately labelled with this number. A record book should be kept for this purpose, should show the number of the sample, date of receipt, name of mine, company or individual from whom received, the gross and net weight, as well as notes on the general mineral character, etc., etc.

Moisture Sample. Assays and chemical determinations are always made on dry samples and the value of a lot of ore is always figured on the moisture free basis. Except in cases when the entire lot may be dried, it is necessary to take a sample from which to determine the moisture. This sample must be taken as quickly as possible after the ore is weighed. If the ore may be quickly crushed and sampled to a small amount of 12 or 14 mesh material, the moisture sample should be taken from this and put in a closely covered pail or box. Duplicate samples of one or more kilograms of this are weighed out into a porcelain or enamelled iron dish and dried at 110° C. The loss of weight being called moisture. As the sample is handled more than the reject, it loses some moisture enroute and a constant should be added to compensate for this difference. Brunton[1] finds 10 per cent in summer and 7 per cent in winter a fair average figure. For instance, if the sample showed 5 per cent moisture for a lot of ore shipped during the summer months a fair figure for the actual moisture content would be 5.5 per cent.

Operations.

Ore sampling may usually be considered to consist of three distinct operations repeated as many times as necessary. These operations are 1st, *crushing;* 2nd, *mixing;* 3rd, *cutting.* After the cutting we have a sample and a reject. The sample may be further reduced by a repetition of the three operations until it has reached the desired bulk.

The whole science of ore sampling depends primarily on a correct knowledge of the proper relation between the maximum size of the ore particles and the weight of the sample taken. The problem to be solved in each case is something as follows:—having crushed a particular ore to a certain size (say 10 mesh), how small a sample is it safe to take from this and still keep within the limit of error allow-

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[1] T. A. I. M. E. XL pg. 567. (1909)

able? It is necessary to know the ore, the limit of error allowable, and the mathematical principles involved.

Sampling is classed as *hand sampling* when the mixing and cutting down is done by men with shovels and as *machine sampling* when done by some form of automatic machine.

Crushing. All the of ore, unless already fine enough, is broken or crushed to pass some limiting size screen. This size depends upon the value of the ore and other factors to be considered later. The finer the pulp is crushed the more uniform in size are the particles and more thorough mixing and better sampling is possible. If the ore is to be smelted, most of it should be left in the coarse state as fine ore is undesirable. If it is to be roasted or leached, on the other hand, fine ore is not objectionable, and the first crushing may be carried further. As a rule, however, the aim is to minimize the crushing, thus saving in cost and keeping down the dust.

Machines for crushing should be rapid in action and capable of easy cleaning. Jaw breakers and rolls fulfil these requirements, ball mills and pebble mills do not.

Mixing. This step in the process of sampling is often omitted or allowed to be taken care of itself. It is a necessary forerunner of quartering and channeling, but is usually omitted before the other methods of cutting. Especially in the handling of small lots of ore in the laboratory, it is best to be over careful in this particular rather than the reverse, and, as it adds but little labor, to give each lot of crushed ore a thorough mixing before cutting.

The four following methods are used in assay office sampling, some being better suited for large lots and some for small lots.

1. *Coning.* The sample is shovelled into a conical pile, each shovelful being thrown upon the apex of the cone so that it will run down evenly all around. In mixing a large lot of ore by coning, it is first dumped in a circle and then coned by one or more men who walk slowly around between the cone and the circle of ore. The best results are obtained by coning around a rod, as by this means the center of the cone is kept in a vertical line. Coning does not thoroughly mix an ore, but rather sorts it into fine material which lies near the center and coarser which rolls down the sides of the cone. If the ore is practically uniform in size, and specific gravity, the mixing may be more thorough. A slight dampening of the ore is said to allow of better mixing by coning. The floor for this and other hand

sampling operations should be smooth and free from cracks which would make good cleaning difficult or impossible. A floor made from sheet iron or steel plates is preferable.

2. *Rolling.* For lots of 200 pounds or less the method of mixing whereby the ore is rolled on canvas, rubber sheeting or paper is often used. When the ore particles are fairly uniform in size and specific gravity, this method is satisfactory, but for ordinary ores in the coarse state, it should be avoided. For ore crushed so fine that it has little or no tendency to stratify, as for example the assay pulp ground to 100 or 120 mesh, the method has been found satisfactory when the operation is properly performed. This method is almost universally used by assayers for mixing the final lot of pulverized ore just before taking out the assay portion.

3. *Pouring.* For small samples the method of pouring from one pan into another is sometimes employed, especially as a preliminary to riffle cutting. Like the two above, it is imperfect when performed on ordinary coarse and fine ore mixed.

4. *Sifting.* For mixing small lots of ore or fluxes the method of sifting is particularly good. The apertures in the sieve should be two or three times as large as the largest particles. The ore should be placed on the sieve a little at a time and allowed to fall undisturbed into a flat receiving pan until all the ore has passed the sieve. Two or three siftings are equivalent to 100 rollings. Sifting has the further advantage over all the other methods that all lumps are broken up and the ore composing them distributed.

Cutting. The final step in the sequence of sampling operations consists in taking out a fraction of the whole, say one-quarter or one-half, in some systematic impartial manner. The part taken out is called the sample and the operation of taking it is the cutting.

The four following methods of hand cutting are used considerably, but some of them are giving way to machine sampling methods.

1. *Fractional Selection.* This is a rough starting method suited only to large lots of low grade or fairly uniform ore. When the ore is being taken away from the crusher or shovelled out of cars as the case may be, every second, third, fifth, tenth shovelful, depending on the value and uniformity of the ore is taken and placed in a separate pile which is afterwards cut down by some of the later described

methods. When shovelling the ore, care must be taken that each shovelful is taken from the floor. In case the ore contains lumps too large for the shovel, they should be broken and put back on the pile. The method is open to the serious objection that it is a very simple matter for a prejudiced party to make the sample either higher or lower in grade than the average by selection of his shovelful samples.

2. *Channeling.* This consists in spreading out the crushed and mixed ore in a flat layer a few inches thick and then taking the sample out in parallel grooves or channels across the pile˙ Often two sets of channels are made one set at right angles to the other. Channeling is a slow method, requiring much labor and floor space, and owing to the coarse pieces which fall into the channels from the sides it is inaccurate. The method is fast falling into disuse.

3. *Quartering.* This is the method of cutting which accompanies coning. It presupposes a thorough mixing by coning, as the two always go together.

When the cone is completed, it is worked down into the form of a flat truncated cone by men who walk around and around drawing their shovels from center to perifery, or by starting at the apex and working the shovel up and down in the path of a spiral. The point to be observed here is not to disturb the radial distribution of the coarse and fine ore. After flattening, the cone is divided into four 90 degrees sectors or quarters by means of a sharp edged board, or better by a steel bladed quarterer. These quarters should of course radiate from the position of the center of the original cone. Two opposite quarters are taken out and rejected and the two others are then taken for the sample. This sample may be again mixed by coning and quartered, or crushed, coned and quartered as the case may require.

When properly carried out the method may be made to yield fairly accurate results, but at best it is a slow and tedious process, and requires the most conscientious work on the part of the laborers to insure correct results. It is open to the objection that it affords opportunity for manipulation of the sample by dishonest operators.

Coning and quartering is the old Cornish method of ore sampling and was almost universally used 30 years ago. It is still somewhat used as a finishing method at sampling works and by engineers in the field where no machinery is available.

4. *Riffle Cutting.* Riffle cutting or splitting is the most accurate laboratory method available. The riffle, splitter or split-shovel

consists of a number of parallel troughs with open spaces between them, the spaces being usually the same width as the troughs. These troughs are rigidly fastened and the whole is made into the form of a shovel, called a split shovel. The ore is taken up on a flat shovel or special pan and spread over the troughs, care being taken to prevent heaping the ore above the troughs. Either the ore which falls in the troughs or that which falls between them may be taken as the sample. The cutting may be repeated as many times as is deemed desirable. For the best results in cutting any sample of ore by this method, care should be taken to have only a thin stream of ore falling from the pouring pan and to move this pouring pan back and forth over the split shovel in a horizontal direction perpendicular to the riffles, so that every part of the stream of ore is being directed alternately and rapidly first into the sample and then into the reject. The more irregular in size, specific gravity and value are the minerals, the greater the care which should be taken in this particular. The sample should be mixed before re-cutting.

A modification of the riffle or split-shovel known as the Jones Sampler or simply as a "splitter" has recently come into use. It is a riffle sampler in which the bottoms of the riffles are steeply inclined, first in one direction and then in the other. The ore is spread over the riffles in the Jones Sampler exactly as over the split-shovel. The ore is caught in two pans placed underneath the splitter.

Riffle cutting is the most rapid method of hand sampling and is also the most accurate. It is used as a finishing method in most modern sampling works. One objection to the Jones Sampler and other similar models is the considerable amount of fine ore-dust which may be lost due to the greater length of fall of the ore before coming to rest. One way to obviate this would be to slightly moisten the thoroughly mixed ore before cutting.

In selecting a split-shovel or riffle cutter for any particular sampling operation, care should be taken that the distance between the riffles be at least three times the diameter of the maximum particle of ore. It is found that a slight bridging action may occur if this precaution is not observed.

Machine Cutting. A large number of machines have been devised to take the place of the slow laborious methods of hand sampling. They all depend on taking the sample from a stream of falling ore. All these devices for sampling fall either under the head of *continuous* or *intermittent* samplers. The *continuous* samplers take *part* of the *stream all the time* by placing a partition in the falling stream of ore to separate sample from reject. The *intermittent* samplers, as the name implies, deflect the entire stream at intervals to make the sample.

The continuous method of sampling is open to the objection that it is impossible to get a stream of falling ore containing coarse and fine particles which is uniform across its entire section. Therefore, any continuously taken sample (except possibly one-half of the stream) will be either richer or poorer than the average. Because of these conditions this type of sampler will not give uniformly reliable results, and is now but little used.

The intermittent method of sampling gives better results. The machine should be so designed that it takes equal portions all across the stream at regular intervals. While it is not possible to produce a stream of ore which is uniform in value throughout its entire length, yet by taking a large number of small samples entirely across the stream the average thus obtained gives a good representative sample of the entire lot. It is essential that the percentage of sample taken from all parts of the delivery pipe be the same, in other words that the vertical sample section, taken in a direction parallel to the motion of the intake-spout should be a rhomboid.

Three machines of this type have come into general use; these are the Brunton, the Vezin and the Charles Snyder. The Brunton oscillates in a vertical plane through an arc of 120 degrees and by a change of gears any proportion of the stream from 5 per cent to 20 per cent may be taken. The Vezin and Charles Snyder machines have sector shaped sample cutters radiating from a shaft around which they revolve.

Hand and Machine Sampling Compared. In comparing hand and machine sampling it may be said that machine sampling is generally cheaper and with a properly designed machine it is more accurate than coning or fractional selection. Perhaps the most important advantage of all is that being strictly mechanical in operation it affords less opportunity for manipulation of the sample.

Precaution to be Observed. Besides the danger of "salting" from crushing machines, elevators, sampling machines etc. special attention must be paid to the disposition of the fine ore dust. As a rule the rich minerals in the ore are more brittle than the gangue with the result that the ore dust is far higher in grade than the average of the ore. Whence is seen the necessity of preserving all of the ore dust and of taking pains to see that the sample contains its proper proportion of the same

Theoretical Considerations. The most certain method of obtaining a representative sample of a lot of ore would be to crush the whole to 100, 120 mesh or finer, mix it thoroughly and then cut down by one of the methods just described. This method can be followed for small amounts of a pound or so, but in the case of large lots, it would entail too much labor and would usually unfit the ore for future treatment. The method generally adopted is a compromise and consists in crushing the whole lot to a certain predetermined maximum size and then taking out a certain fraction as a sample. This sample is again crushed to a smaller size and cut down as before and this process repeated until finally the assay sample is obtained.

The care which is required in sampling as well as the size to which a lot of ore or other material must be crushed before a sample is taken depends upon the value and uniformity of composition of the material. The more uniform it is, the smaller may be the sample taken after crushing to any particular size. For instance, if we have a solid piece of galena containing silver uniformly distributed as an isomorphous silver sulphide, we can break off a piece anywhere, crush it and have for assay a lot of ore which is truly a sample of the piece. If, however, our specimen is not solid galena, but is made up of galena and limestone, the silver value still being contained in the galena, we will have to crush the whole lot to a uniformly fine size before taking out a fractional part for a sample. Furthermore it will readily be seen that the greater the difference in the grade of the different minerals in the ore, the finer must a lot of ore be crushed before a certain sized sample should be taken from it.

Since ores are never perfectly uniform in composition a certain amount of crushing is evidently necessary in every case. To determine the amount of crushing we must first consider the commercial side of the question, that is we must determine how far it will pay to go with the process. Evidently a mistake of 1 per cent in the iron contents of a car load of iron ore worth say $3.00 a ton is less serious than the same percentage error in the copper contents of a car of copper ore worth say $50.00 a ton. Therefore it may be seen that it will pay the seller or buyer of the copper ore to go to more pains and expense in the sampling of the ore than if he were dealing with the less expensive iron ore.

Varying Relation of Size of Sample to Maximum Particle. The variation of any portion of a lot of ore from the average composition of the whole is due to the excess or deficit of one or more particles. The effect upon the results will be greatest when the piece or pieces which are in excess or deficit are of the largest size, greatest specific gravity and greatest variation in quality from the average.

Disregarding for the moment the last two of these factors and supposing the ore particles to be approximately uniform in size it is evident that the sample must contain enough particles so that one additional particle of the richest mineral would practically cause no variation in the value. This means that the sample of the ordinary ore must contain a very large number of particles perhaps 500,000.

Having determined how many particles of the ore it is necessary to include in the sample, and assuming the different minerals to be entirely detached from one another, it would be fair to take such a weight of ore after each reduction as would contain this established number of particles. Or as the weight of a lump is proportional to the cube of its diameter we may state the rule as follows:—Make the weight taken for the sample proportional to the cube of the diameter of the largest particle of the ore.

In the ordinary ore, however, the different minerals are not entirely detached from each other, but approach more and more to this condition as the size of the ore is reduced. Hence a fixed number of the particles of the fine ore is less likely to be a true average of the whole than the same number of pieces of the lump ore before it was broken. Therefore as the size of the ore is reduced a larger and larger number of particles should be taken for the sample. To conform to this condition of affairs the following rule was proposed by Professor R. H. Richards: "For any given ore the weight taken for a sample should be proportional to the square of the diameter of the largest particle."

The accompanying table embodies this rule and is based on figures taken from the practice of several careful managers. It was arranged and is now published with the permission of Professor Richards.

The first column shows the safe weight in pounds for a sample of ore of any of the six grades shown and for sizes as indicated in the respective columns. Column 1 applies to iron ores, column 2 to low grade lead, zinc and copper ores and even to low grade pyritic gold ores, without native gold, where the pyrite is evenly distributed through the ore. Columns 3 and 4 apply to ores in which the valuable minerals are less uniformly distributed. Columns 5 and 6 apply to ore containing fine particles of native gold or silver, also to telluride and other "spotty ores."

TABLE IV. WEIGHTS TO BE TAKEN IN SAMPLING ORES.

Weights of Sample Pounds.	1	2	3	4	5	6
	Diameter of Largest Particles Millimeters.					
	Very Low Grade or Very Uniform Ores.	Low Grade or Uniform Ores.	Medium Ores.		Rich or Spotted Ores.	Very Rich and Spotted Ores.
20,000.000	207.00	114.00	76.20	50.80	31.60	5.40
10,000.000	147.00	80.30	53.90	35.90	22.40	3.80
5,000.000	107.00	56.80	38.10	25.40	15.80	2.70
2,000.000	65.60	35.90	24.10	16.10	10.00	1.70
1,000.000	46.40	25.40	17.00	11.40	7.10	1.20
500.000	32.80	18.00	12.00	8.00	5.00	.85
200.000	20.70	11.40	7.60	5.10	3.20	.54
100.000	14.70	8.00	5.40	3.60	2.20	.38
50.000	10.70	5.70	3.80	2.50	1.60	.27
20.000	6.60	3.60	2.40	1.60	1.00	.17
10.000	4.60	2.50	1.70	1.10	.71	.12
5.000	3.30	1.80	1.20	.80	.50	
2.000	2.10	1.10	.76	.51	.32	
1.000	1.50	.80	.54	.36	.22	
.500	1.00	.57	.38	.25	.16	
.200	.66	.36	.24	.16	.10	
.100	.46	.25	.17	.11		
.050	.33	.18	.12			
.020	.21	.11				
.010	.15					
.005	.10					

It should be remembered that the above mentioned rules for sampling will not hold for ore containing large pieces of malleable minerals such as native gold, silver, silver sulphide, chloride etc. These roll out and do not crush and must be treated by special methods. See "Sampling Ores Containing Malleable Minerals."

In using the table, it is not necessary to crush successively to all of the sizes shown in any of the columns. The ore may be crushed to any fineness convenient and then a weight of sample corresponding to that shown in the table may be taken. In sampling mill practice it is customary to reduce the diameter of the coarsest particles one-half at each stage or crushing, thus reducing the volume to one-eighth or 12.5 per cent. It is also customary in practice to take a 20 per cent sample at each stage, consequently the ratio between the weight of sample and size of maximum particle is constantly increasing throughout the sampling process, thereby meeting theoretical conditions previously discussed.

Relation of Size of Sample to Grade of Ore and Effect of Specific Gravity of Richest Mineral. Although it had long been appreciated that the size of the sample would have to be greater as the richness of the ore increased, it remained for Reed[1] to develop a formula by which the proper ratio between these could be scientifically maintained.

D = diameter of largest pieces in inches.
P = quantity of the lot in Troy ounces.
f = number of parts into which P is to be divided before one part is taken as a sample.
k = percentage of silver or gold in the richest specimens in the lot.
s = specific gravity of the richest minerals.
m = average grade of ore (ounces per ton).
a = number of pieces of D size and k value that can be in excess or deficit in the portion chosen as sample.
l = largest allowable percentage of error.

Before taking a sample of $\frac{1\,P}{f}$ Troy oz. we must crush the lot so that

$$D = .05\sqrt[3]{\frac{mPl}{sk(f-l)a}}$$

Taking for general purposes s = 7, l = 1 and a value of *a* of 1.6, the following table is given for different grades:

Medium	m = 50	k = 1
High grade	m = 75	k = 10
Very rich	m = 500	k = 30

TABLE V.

Sample reduced from	Value of D in inches.		
	Medium	High Grade	Very Rich
100 to 10 tons	5.28	2.96	2.53
10 to 1 ton	2.46	1.38	1.2
2000 to 200 lbs.	1.14	0.6	0.56
200 to 5 lbs.	0.3	0.18	0.16
5 lbs. to 10 assay tons	0.034	0.02	0.018

This quantity assumed for *a* appears to be very small and in the opinion of the writer should be larger, which would have the effect of reducing the values for D shown in the above table.

Brunton[2] derived a formula similar to Reed's but more convenient to use.

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[1] School of Mines Quarterly VI. page 351 (1885)

[2] T. A. I. M.E. XXV. p. 826 (1895)

W = weight of sample in pounds.
k = grade of richest mineral in ounces per ton.
c = average grade of ore in ounces per ton.
s = specific gravity of richest mineral.
n = number of maximum sized particles of richest mineral in excess or deficit in sample.
f = a factor expressing the ratio of the actual weight of the largest particle of richest mineral which will pass a screen of a given size to the weight of the largest cube of the same mineral which will pass the screen.
p = allowable percentage error in sample.
D = diameter in inches of the holes in the screen, or other normal diameter to which the ore is crushed.

From these he finds

$$D = .65 \sqrt[3]{\frac{Wcp}{fsn(k-c)}}$$

Making p, the allowable percentage error, = 1, the formula becomes:

$$D = .65 \sqrt[3]{\frac{Wc}{fsn(k-c)}}$$

To determine a value to use for *n* Brunton made a number of assays on two different lots of high grade ore crushed to pass a certain limiting screen. The average deviation from the mean = p was substituted in the formula and results of 2.64 and 3.14 respectively were found for n. Assuming that 3 is a safe value for n and cubing each side we find.

$$D^3 = \frac{Wc}{10.8\ fs(k-c)}$$

or

$$W = \frac{10.8fsD^3(k-c)}{c}$$

from which may be found the safe weight in pounds for a sample of any ore whose largest particle is D inches. Taking four examples using as the richest minerals pyrite, galena, native silver and native gold and assuming different values for D, k, c and f the following table was made after the style of the table first shown in Hofman's Metallurgy of Lead. The values for f used for the fine sizes were those determined by Brunton's experiments, i. e. 4 for pyrite and galena and 6 for native silver and gold. This value of f is reduced gradually until for 1 inch diameter, it is made equal to one, this variation therefore tending to compensate for the greater uniformity of value of the particles as they become larger.

This following table is probably the best and certainly the most conservative of all. A good deal of intelligent discrimination may often be used however and mere formula can never be made to cover all possible contingencies. For instance in sampling an ore in which the valuable mineral is finely and uniformly disseminated throughout the gangue, a much smaller sample than that given in the table may be taken for the coarse sizes, although for the fine sizes the full quantities shown in the table should be taken. Another ore, with perhaps the same ratio of value of the richest mineral to average grade, having the rich mineral in larger crystals or masses will have to be sampled

TABLE VI. WEIGHTS TO BE TAKEN IN SAMPLING ORE.

Specific Gravity Richest Mineral	Size of Particles.		Safe Weight in Pounds when Largest Particles are of Size Given in Second Column.					
			Grade of Richest Mineral Divided by Average Grade.					
	Mesh	Diam. Inch	10	50	200	600	1500	2500
5.0	120	.0043			.003	.010	.025	.043
	100	.0055	.0003	.0018	.007	.021	.053	.089
	50	.0100	.0017	.0095	.039	.116	.291	.485
	14	.0364	.0585	.319	1.29	3.90	9.76	16.3
	4	.1450	2.96	16.13	65.5	195.	494.	823.
	2	.338	30.03	163.5	663.9	1998.	5000.	8337.
		.5	75.9	413.	1679.	5054.	12648.	21095.
		1.0	486.	2646.	10746.	32346.	80946.	140346.
7.5	120	.0043			.005	.015	.038	.064
	100	.0055	.0005	.0027	.011	.032	.080	.134
	50	.0100	.0026	.0143	.058	.174	.437	.727
	14	.0364	.0878	.479	1.94	5.85	14.64	24.5
	4	.1450	4.44	24.2	98.3	293.	740.	1234.
	2	.338	45.0	245.	996.	2997.	7500.	12505.
		.5	114.	620.	2519.	7581.	18972.	31643.
		1.0	729.	3969.	16119.	48519.	121419.	210519.
10.5	120	.0043	.0005	.0027	.011	.032	.081	.135
	100	.0055	.0010	.0055	.022	.068	.170	.283
	50	.0100	.0041	.0222	.090	.272	.679	1.133
	14	.0364	.1476	.804	3.26	9.83	24.59	41.00
	4	.1450	7.78	42.35	172.0	517.7	1295.	2160.
	2	.338	78.8	429.	1742.	5245.	13126.	21883.
		.5	230.	1250.	5077.	15283.	38247.	63762.
			1500	3000	6000	15000	30000	60000
17.6	150	.0036	.0798	.159	.319	.798	1.59	3.19
	120	.0043	.1359	.272	.544	1.36	2.72	5.40
	100	.0055	.284	.569	1.138	2.84	5.69	11.38
	50	.0100	1.14	2.28	4.56	11.4	22.8	45.6
	14	.0364	41.2	82.5	165.	412.	825.	1650.
	4	.1450	2172.	4346.	8692.	21716.	43461.	86922.
	2	.338	22004.	44037.	88074.	220038.	440370.	880740.

as carefully as indicated by the table throughout the entire operation.

It should also be noted that except in the case of native metals the richest minerals are usually more finely divided by crushing than the gangue so we seldom have the extreme case provided for by the formula.

One of the most difficult things an assayer may be called upon to do is to sample such a mill product as vanner concentrates. In these the particles of gangue minerals are two or three times the diameter of the average rich mineral and good mixing is impossible. The material stratifies on the slightest provocation and the greatest care must be taken if the sampling is to be successful.

Duplicate Sampling. To check the accuracy of the sampling operations, we may resort to the process of duplicate sampling or to re-sampling. Duplicate sampling in the laboratory should consist in first cutting the entire lot into two portions and then sampling each one down separately. The results should check usually within one per cent. If not, it indicates either poor mixing and cutting or a too rapid reduction of sample.

Some sampling mills are arranged to allow for taking duplicate samples so that they have constant checks on the accuracy of their sampling operations. The following results of assays made on original and re-sampled lots are taken from D. K. Brunton's paper on Modern Practice of Ore-Sampling in the Transactions of the American Institute of Mining Engineers[1] and shows how closely such work is made to check.

TABLE VII. RESULTS OF RE-SAMPLING.

Lot No.	Sample Gold. Ounces per ton	Re-sample Gold. Ounces per ton
3192	3.62	3.64
3198	5.04	5.015
3219	2.70	2.67
3235	3.18	3.16
3310	1.17	1.17
3324	6.52	6.51
3340	0.71	0.78
3388	1.70	1.84
3424	9.24	9.20
3471	30.64	30.52

Finishing the Sample.

When the sample has been reduced to a few pounds of 40 or 50 mesh ore, from one to five or more pounds depending on the character

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[1] T. A. I. M. E. XL. p. 567 (1909)

of the ore, is ground to 120,150 mesh or finer. This final grinding may be done on the bucking board or in any of the numerous forms of sample grinders. As the sample grows smaller more and more care has to be taken to prevent contamination or "salting." A few particles of rich ore, which if introduced into the original lot, would have had no material effect on the average might easily seriously alter the result if allowed to enter the final sample.

The grinding machines, sieves etc. should be so constructed that they may be easily and thoroughly cleaned. Many excellent pulverizers are unsuited for sampling work on account of the labor and difficulty of effective cleansing. One of the best methods of cleaning the bucking board or sample grinder is to brush out, then grind a quantity of some barren material such as sand or crushed fire-brick and follow this by a second brushing. All split-shovels, brushes, screens and rolling cloths must also be carefully cleaned before use.

Before commencing the final pulverizing, the sample should be thoroughly dried by heating to 100° or 110° C. No greater degree of heat than this should be used as there is danger of roasting the sulphides or otherwise altering the composition of the ore.

Size of Assay Pulp. For assay purposes, all ore should be reduced to at least 100 mesh and rich spotty ores should be pulverized to 120 or 140 mesh or finer to insure a fair sample being obtained for the final crucible or scorification assay. For a crucible assay using 1 assay-ton an ore may be left coarser than for a scorification assay where only 0.1 assay-ton charge is used. If the assayer has difficulty in obtaining results checking within one-half of one per cent he may well look for the difficulty in the size of the assay pulp. Very often a regrinding to a finer size will overcome the difficulty.

When any portion of ore has been selected as a sample and is to be passed through a sieve, it is essential that the whole sample be made to pass. The harder portions which resist crushing the longest are almost invariably of a different composition from the remainder and if rejected render the whole sample worthless.

Ores Carrying Malleable Minerals.

In crushing ores containing metallic particles and other malleable minerals more or less of those will be left on the sieve as flat scales, cylinders or spheres. When such an ore is being sampled the particles found on each sieve must be separately preserved and weighed and a careful record made of the weight of the original ore and of each of the cuts throughout the sampling process. If the pellets are gold or silver, they are wrapped in lead foil and cupelled, weighed and parted. If of copper, as in the case of an ore containing native copper, the weight of the metallic contents is otherwise established, perhaps by cleaning in hydrochloric acid and direct weighing or by making a fusion as in the copper assay.

The following example shows how with the above data and the assay of the fine ore the assay value of the original sample is calculated. It may be either higher or lower than the fine ore. One assumption has to be made in all such cases and that is that the reject contains the same proportion of pellets as the sample. It need hardly be mentioned that if the proper ratio between size of sample and maximum grain has been maintained the above assumption will be born out in practice.

CALCULATION OF ASSAY WHEN ORE CONTAINS COARSE PARTICLES OF NATIVE GOLD.

Data.

A sample of 23.95 kilograms or 23,750 grams was crushed to pass a 40 mesh–sieve.	– On sieve 25 grams. This yielded 6.2750 grams of gold. – Through sieve 23,600 grams (Loss 125 grams). A sample from this of 5825 grams was crushed–to pass a 120 mesh seive.	– On sieve three grams. This yielded 1.6720 grams of gold. – Through sieve 5802 grams (Loss 20 grams). The fine ore assays 1.20 oz. gold per ton.

Calculations. Wt. Gold

Total pellets from 23,750 grams of ore on 40 mesh 6.27500 grms.

Total 40 mesh ore assuming loss to be same as the rest i.e. sample now 23,725 grams.

Total pellets from 23725 grams on 120 mesh

$$= \frac{23725}{5825} \times 1.6720 = \qquad 6.81006$$

Assuming all of ore to be crushed through 120 mesh

$$\text{and no loss there would be } 23{,}725 - \frac{23725}{5825} \times 3$$

= 23,713 grams fine ore (assaying 1.21 oz.)

$$\text{Total gold in this} = \frac{23713 \times .00121}{29.166} = \qquad 0.98146$$

Total gold in original lot 14.06652

$29.166 : \times = 23750 : 14.06652$

$\times = .01727$ = Au from 1 assay-ton

Ore assays 17.27 oz. per ton.

CHAPTER IV.

BALANCES AND WEIGHTS.

The reliability of every assay or other quantitative determination is directly dependent upon the accuracy of the weighing, both of the ore charge and more especially of the resultant product, for example, the silver button or the parted gold. Any error made in the weighing will, of course, invalidate all the rest of the work regardless of any amount of care which may have been given it. The operator should, therefore, familiarize himself with the construction, sensibility and operation of his balance before he attempts to do any accurate assaying.

A good assay balance with careful and intelligent use is capable of weighing to 0.01 milligram or 0.00001 gram. For the most delicate assay balances an accuracy of 0.000002 gram is claimed. The necessity of weighing to this degree of accuracy may be understood when it is considered that taking the usual charge of ore, 1 assay-ton, (29.166 gms.) or about an ounce, that in weighing the resultant gold to the nearest 0.01 milligram the value of the ore is only determined to within 20 cents per ton. This is usually sufficiently close, but any less degree of accuracy would not be so considered.

At least three grades of balances are necessary for the fire assay laboratory, these are known as flux, pulp, and button or assay balances. In large assay laboratories, there are also usually found bullion and chemical balances as well as separate assay balances for gold and for silver.

Flux Balance. The flux balance for the weighing of fluxes, reagents, etc. should be an even balance scale, provided with a removable scoop-shaped pan capable of weighing 2 kilograms and sensitive to 0.2 gram.

Pulp Balance. The pulp balance for weighing the ore or pulp for assay and the buttons from lead assays etc. should be an even balance scale. The pans should be made removable and should each have a capacity of at least 2 ounces of sand. It should be enclosed in a glass case and should be sensitive to one milligram. Such balances are usually listed in the manufacturers' catalogue as prescription balances and may be purchased for $20 or $25. If more than one pulp balance is to be obtained, it is well to get one or more having a pan capacity of 4 or 5 ounces of sand. For ½ and 1 assay-ton charges the two ounce pan is to be preferred as it is easier to transfer ore from it to the crucible than with a larger pan.

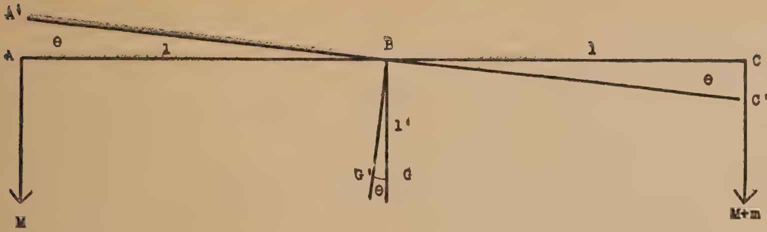
Button Balance. The button or assay balance is the most sensitive balance made. It should be capable of weighing to at least 0.01 milligram, should be rapid in action, making a complete oscillation in from 10 to 15 seconds, and should have stability of poise, that is to say that it should be so made that its adjustments will not change sensibly from day to day owing to slight changes of temperature and atmospheric conditions. The capacity of the assay balance need not be large, 0.5 gram maximum is sufficient, but the beam should be rigid at this load.

Such a delicate piece of apparatus must be handled with great care if good service is expected of it. It should be as far as possible from any laboratory or part of the plant where corrosive fumes are being evolved, and should be covered when not in use to keep out the dust.

The balance beam should be as light as possible consistent with the necessary rigidity. For this reason the truss frame construction is usually adopted, giving the maximum strength with the minimum weight. The construction should be such that the two balance arms are of equal weight and length and the three knife-edges should all lie in the same plane. The material of the beam should be non-magnetic for obvious reasons and should have a small coefficient of expansion. The knife-edges and bearings should be of agate, ground and polished. The knife-edges should be so sharp that a strong pocket-lens will show no flatness on the bearing edge. All of the metal work of the balance should be protected from attack by chemical fumes by some such means as gold-plating or lacquering. Lacquering seems to resist chemical fumes rather better than the ordinary gold-plating. The construction of the balance should be such that the rider may be placed on the zero graduation and used from the zero point to the end of the beam.

The balance must be mounted in such a way that it will be free from vibration. Such a support may be obtained by placing the shelf on which the balance rests, on one or more posts which are set in the ground and which come up through the floor without touching it.

Theory of the Balance. The balance is essentially a light trussed beam, supported at its center by a knife edge. At each end is hung a scale-pan, both of which should be of equal weight.



Let the three knife-edges A, B, and C be in the same straight line. Let AB = BC = l. Let G be the center of gravity of the beam whose weight is W. Let the distance of the center of gravity below the point of support, BG = l'.

With a load of M in each pan there will be equilibrium. Now if a small weight (m) be added to the right-hand pan, the balance will swing through a small angle θ and the beam will again come to equilibrium in a new position A'BC'. The condition for equilibrium will be obtained by taking the moments of the three forces, M, M + m and W about the axis B. This gives the relation:

$$Ml \cos \theta + l' \sin \theta\, W = (M + m)l \cos \theta$$

$$\text{or} \quad \frac{\sin \theta}{\cos \theta} = \tan \theta = \frac{lm}{Wl'}$$

The sensitiveness of a balance is usually denoted by the angle through which the beam will swing when a small weight usually 1 milligram, (for assay balance 0.1 milligram) is added to one pan. For small angles the tangent and its angle may be taken as equal and therefore the expression deduced for tangent θ above may be taken as a measure of the sensitiveness of the balance.

The equation for tangent shows that the sensitiveness of a balance varies:

(a) Directly as the length of the balance arms.
(b) Inversely as the weight of the beam.
(c) Inversely as the distance of the center of gravity below the point of support. (Distance BG.)

The sensitiveness is seen to be independent of the load if the three knife-edges are in the same straight line and most balance makers attempt to approach this condition in making assay balances. When B is above AC the sensitiveness is decreased with the load, when B is below AC it is increased up to a certain limit, beyond which the equilibrium becomes unstable.

The condition of increased sensitiveness with long beam and small weight ((a) and (b) above) conflict, as the longer the beam is made the heavier it must be. The length of the arm is also limited by the time of swing of the balance which may be considered to be a compound pendulum. A period of about 10 or 15 seconds is about the time required for a complete oscillation. Formerly the long arm balances were common but at present the makers are restricting the length of the beam to 4 or 5 inches.

By bringing the center of gravity nearer to the center of support the sensibility is increased. As the center of gravity nears the center of support, the stability of poise decreases until when the two coincide there would be no point of rest and the balance would be unstable or "cranky." The most difficult thing to obtain is a balance with great stability and extreme sensibility. It is obtained by making the beam as light as possible and then keeping the center of gravity sufficiently below the center knife edge to give the necessary stability. Most high grade balances are provided with a screw-ball or sliding-weight so that the center of gravity may be adjusted. If the balance lacks stability, i.e. is cranky and over-sensitive, both of those conditions may be reduced by lowering this weight and thus lowering the center of gravity of the system.

In the above discussion the assumption has been that the arms of the balance were equal. Modern high grade balances usually approach very closely to this condition. The process of *double weighing* serves to eliminate, however, any error in weighing that may be due to such inequality. Call the observed weight of the body as weighed in pan A, W', and that in pan C, W''. Then W the true weight is found as follows:

$$W = \sqrt{W' W''}$$

when W' and W'' are nearly equal $W = \sqrt{2}\ (W' + W'')$

General Directions for the Use of the Balance

1. Note the maximum load the balance will carry and do not exceed this.

2. The balance should be put into action by gently lowering the beam onto the knife edges.

3. Have the amplitude of swing not more than 3 or 4 divisions each side of the center.

4. Arrest the swinging of the balance when the pointer is at the center of the scale.

5. Turn the balance out of action before adding to, or taking weights from the pan.

6. When not in use raise the beam off the knife edges and leave the rider on the beam.

7. The final weighing must be made with the case closed.

8. Weights should be placed only in the box or on the scale pan and should be handled only with the forceps.

9. Record the weight of the substance; first by noting the weights which are absent from the box, second by checking off each weight as it is put back in the box.

Weighing.

Brush off the balance pans and if necessary clean off the front plate of the balance. Adjust if necessary and try the adjustment each time you have any weighing to do. In putting the balance into action it may start swinging slightly of its own accord. If it does not, set it swinging by gently fanning one pan with a motion of the hand, or by lifting the rider for an instant and then putting it back on the beam. A device such as a medicine dropper may be used for starting the balance swinging by blowing with it gently on one pan. If the balance is started swinging by fanning with the hand it should be allowed to make one or two complete oscillations before a reading is taken, to prevent air currents from interfering with the normal swing.

In reading the position of the pointer on the ivory scale, arrange always to have the reading eye in the same position relative to the ivory scale, that is in a plane perpendicular to the scale and passing through the center graduation. A mark may be made on the glass door by which to line up the eye before each reading.

Each silver bead should be placed on its side on a small anvil, hammered and then brushed before it is weighed.

To transfer the gold from the parting cup to the scale-pan take the scale-pan with the forceps and place on the front part of the glass mounting base. Gradually invert the parting cup over it tapping it gently. The gold should all slide into the pan. Any particles adhering to the cup may be detached by touching gently with the point of the forceps or by means of a small feather trimmed to a point.

Before weighing the gold, examine it carefully to see if it is clean and remove any foreign matter if present.

For ordinarily accurate commercial work the weighing of the gold and silver is done by the "*method of equal swings*" using the rider for the final weighing. For extreme accuracy as for instance in the callibration of weights, the weighing is done by "deflection" also called the "*method* of *swings*."

Weighing by Equal Swings. First of all the balance is adjusted by the star wheel or preferably by the adjusting rider, if one is provided, until the needle swings exactly the same on each side of the center, reading always in the same order, say from left to right. For accurate gold weighing it will be necessary to estimate tenths of divisions on the ivory scale.

Put the substance to be weighed on the left-hand pan and add weights to the right-hand pan until within a fraction of a milligram of the weight of the substance. The application of the weights should be done in a systematic manner, starting with one which is estimated to be too large. If too large, it is removed and the next smaller weight tried and so on, always working from larger to smaller weights until within 1 milligram of the true weight.

In trying any weight have the balance off the knife edges, put the weight in the pan and gently turn the balance key until the pointer inclines slightly to one of the other side. This swing of only one or two divisions should indicate immediately whether the weight on the pan is too much or too little. Again turn the balance out of action before making any change of weight.

When within a fraction of a milligram of the correct weight, the right hand or weighing rider is shifted about until on putting the balance into action the needle does not move very decidedly in one or the other direction. Then set the beam swinging two or three divisions each side of the center. If it does not swing exactly evenly arrest the swing and change the position of the rider and try again. Repeat until the needle swings exactly the same as when adjusted. After becoming familiar with the balance two or three trials only of the rider will be necessary.

The weight of the substance is found from the sum of the weights on the pan plus the fractional parts of a milligram indicated by the position of the rider on the beam.

Weighing by Method of Swings. First, determine the position of rest of the pointer under zero load by noting the position of the pointer at the extreme swing on each side, taking 3, 5 of a greater odd number of consecutive readings. Call the center division zero and count divisions and estimate tenths to each side, calling those to the left of the center $-$, and to the right $+$.

Example.

	Left		Right
	−3.9		3.6
	−3.7		3.4
	−3.5	2	7.0
3	−11.1		3.5
	−3.7		
	+ 3.5		
2	− .2		
	− .1		Point of rest.

Or the point of rest would be 0.1 division to the left of the center.

Call the point of rest under zero load r. Place the object to be weighed on the left-hand pan and weights on the right-hand pan until equilibrium is nearly established. With the rider determine the weight to the next smaller 0.1 milligram. Set the beam swinging as before and find the position of rest for the pointer. Call it r'. Shift the rider to the right one whole division (= 0.1 mg.) so as to bring the point of rest on the opposite side of r, and find the position of rest again, call it r''. The tenths of a milligram to be added to the weights and rider reading when r' was found is then

$$\frac{r' - r}{r' - r''}$$

For instance let the weights and rider reading be 27.4 mg. and let $r' = -1.4$ and $r'' = +1.6$

then $\dfrac{r' - r}{r' - r''} = \dfrac{-1.4 + 0.1}{-1.4 - 1.6} = \dfrac{-1.3}{-3.0} = +0.43$

and the true weight would be 27.4 + 0.04 = 27.44 mg.

Another method of weighing by "deflection," requiring a knowledge of the sensibility of the balance is as follows. Suppose that a weight of 0.10 milligram will cause a deflection of the point of rest 2.0 divisions on the ivory scale. Adjust the balance so that the point of rest with no load corresponds to the zero of the ivory scale. Place the substance to be weighed in the left-hand pan and again determine the point of rest. Suppose this is 1.2 (divisions). Then the weight of the substance is 0.06 milligrams. With a good balance this is a rapid and accurate method for small amounts of gold but is not very commonly used.

Weighing by No Deflection. A third method of weighing called weighing by "no deflection" is sometimes employed for rough work. It consists in applying the necessary weights and then shifting the rider until the needle shows no deflection when the balance is lowered gently onto the knife edges. This method disregards friction and inertia and is not as accurate as the two previously described methods.

Weighing by Substitution. This method of weighing is the one usually adopted for the standardization or adjustment of weights, as it avoids any possibility of error due to inequality of arms. It consists simply in placing the substance to be weighed on one pan, counterbalancing it with weights placed on the other pan, and then removing the substance and adding standard weights until the balance is again in equilibrium. The weight of the substance being obtained from the substituted weights.

Check Weighing. Students are advised to check all gold weighings in the following manner. Weigh and record weight of each duplicate, then place both buttons or prills on one scale-pan and obtain the weight of the two. Compare this with the sum of the weights obtained in the separate weighings. The figures should check within 0.01 of 0.02 milligram. If not, either one of the weighings is at fault or some of the weights are in error. Check weighing also serves to double the accuracy of the assay and is practised by many of the best assayers.

Adjusting and Testing an Assay Balance.

Levelling. Level the balance by adjusting the footscrews and by observing the plumb-bob of level. Be sure that it rests firmly on the table or other support so that it will not be moved during the test. See that the beam, scale-pans and hangers are in their proper places and not out of normal position due to previous careless usage.

Equilibrium. Lower the beam carefully until the agate knife-edges rest on the agate supports. This motion and the reverse one must be gentle to prevent injury to the knife-edges and also as any shock or jar will tend to change the adjustments. Adjust the balance so that it swings equally on each side of the center. A nut on one or each end of the beam, a star-wheel, a small projecting piece of metal or "flag" revolving on a vertical axis at the middle of the beam, or preferably an extra rider, constitutes the attachment for this adjustment. If this adjustment cannot be made but the balance on starting to one side or the other continues to swing in that direction with increasing velocity, it is in unstable equilibrium, and the center of gravity must be lowered until the proper equilibrium is obtained.

Time of Oscillation. Set the balance in motion and note the time of one complete oscillation, i.e. swing from one extreme to the other and back again. For the modern 4 or 5 inch beam assay balance this should be from 10 to 15 seconds. If much faster than this the balance will probably not be very sensitive. If much slower than this each weighing will take a correspondingly longer time and the balance may lack stability.

Stability. After each of the tests the beam should be lowered and the adjustment of the balance noted. If it no longer swings equally on each side of the center, due care having been taken to avoid disturbing any of the adjustments, it lacks stability. This may be due to its adjustment to a too great degree of sensitiveness which can be overcome by lowering the center of gravity of the system by means of the screw ball, or it may be due to defect in construction, arms of unequal length, etc. in which case it can not be remedied.

Resistance. If the knife-edges are dull or the supporting surfaces rough the frictional resistance to swinging will be considerably and the diminution in amplitude of swing will be rapid. Note the position of the pointer on the scale at the extremes of several successive swings. The difference between successive readings on the same side will show the diminution in amplitude due to friction and to resistance of the air. This should not exceed 0.2 to 0.4 of a division in a good assay balance. The horizontal section of the beam and the area of the pans and other projecting parts should be as small as possible to reduce the air resistance.

Let the balance swing until it comes to rest and read the position of the pointer, lift the balance off of the knife-edges and repeat several times. The positions should not differ by more than 0.05 of a division. This indicates a flatness of the knife-edges or a roughness of the supporting surfaces. If the beam is exceedingly slow in coming to rest this test is unnecessary.

Sensibility. The sensitiveness is defined by physicists as the angle moved through by the beam when 1 milligram excess weight is added to one pan. The angle being proportional to the number of scale divisions passed over, this latter is taken as a measure of the sensitiveness.

From a practical point of view the sensitiveness is the smallest difference in weight which the balance will indicate. Thus, when we say that a balance is sensitive to 0.01 milligram we mean that 0.01 milligram added to one pan will cause a noticeable difference in the swing or in the zero[1] point. With the usual width of graduation of the ivory scale 0.05 inches, the pointer should swing over at least one-fifth of a division for each 0.01 milligram added to the scale-pan, if the balance is to be termed sensitive to 0.01 milligram.

The writer has never seen described a satisfactory practical method of comparing the sensibility of different assay balances, but has used the following method based on the commonly accepted space of 0.05 inches, between the graduations on the ivory scale.

Procedure. Determine the zero point with any given load on the pans, then add 0.10 milligram to the weight on the right-hand side of the beam using the rider and again determine the zero point. Multiply the difference between these two positions (expressed in terms of units of graduation) by the distance apart of the graduations in hundredths of inches and divide by 5.

Comparative sensibility = (deflection of zero due to 0.1 mg.) =

$$\frac{\text{(space between graduations in hundredths of inches)}}{5}$$

Example. Deflection 1.2 divisions, space between graduation 0.05 inches.

Comparative sensibility $\frac{1.2 \times 5}{5} = 1.2$ which means that this balance will weigh to something better than 0.01 milligram.

To Test Equality of Arms. Adjust balance to swing evenly with no load and then place *equal* weights on each pan equivalent to the full load of the balance. If the pointer does not now swing evenly the arms are of unequal length.

To Determine if Knife Edges are all in Same Horizontal Plane. Adjust balance and determine sensibility with no load. Then place full load on each pan and again determine sensibility. When the three knife edges are in the same place there should be no change of sensibility with anything up to the full load of the balance. When the full load of the balance is not known the sensibility should be determined for gradually increasing loads and a curve of sensibility drawn. If the three knife edges are in the same plane this curve should be a straight line up to the point where the beam begins to be deflected by an overload.

[1] zero point = position of the point of rest.

Weights.

For the three balances above described we require four sets of weights, as follows:—

For the *flux balance* we should have a block containing weights from one kilogram to one gram. These weights need not be extremely accurate.

For the *pulp balance* two sets are necessary, *gram* and assay-ton weights: *gram weights*, from 20 grams to 10 milligrams for weighing argols and ore for lead, copper and tin assays as well as the buttons from the same: *assay-ton* weights, 2 A. T. to $\frac{1}{20}$ A. T. for weighing ore, matte, speiss and lead bullion for the gold and silver assay.

For the *button balance* is required a set of milligram weights of the utmost accuracy, from 1 milligram up to 500 or 1000 milligrams. These are preferably made of platinum as an absolutely non-corrosive weight is imperative. *Riders* are used for determining fractions of 1 milligram. Riders are made of fine platinum or aluminum wire and are usually made to weigh 0.5 milligram or 1.0 milligram. The balance beam is divided usually into 100 spaces each side of the center and then when a 1 mg. rider is used each space represents 0.01 milligram.

For many balances a rider with a diamond shaped loop known as the Thompson rider is to be preferred. Its principal advantage is due to its property of always hanging in a vertical position when on the rider arm. Even if it falls over to one side when on the beam it will slip back to the vertical position when lifted by the rider arm. The diamond-shaped loop prevents it from swinging or twisting around on the rider carrier and permits the rider to be placed squarely on the beam.

Multiple Rider Attachment. Some of the balance makers are now supplying on demand what is called a multiple rider attachment designed to do away with the use of the smaller weights. It consists of a carrier supplied with a number of riders of different weights for instance 1, 2, 3, 5, 10, 20, 30 milligrams, so arranged that any of all may be placed on a support provided for the purpose, and which is equivalent to placing flat weights of the same value in the pan.

The advantages claimed for this device are a saving in the wear and tear of weights, as the small flat weights frequently handled by forceps become broken and inaccurate whereas there is practically no wear on the riders so that they will maintain their original weight almost indefinitely. A second advantage claimed is a saving in time as with this attachment the weights may be manipulated much quicker than can the flat weights with forceps. It is not necessary to open the door of the balance in weighing a button under 40 or 50 milligrams and this alone is a saving of some time and also allows all air currents to subside before the final reading is made.

Assay-Ton Weights. The assay-ton system of weights was devised by Professor C. T. Chandler of Columbia University, to facilitate the calculation of results of gold and silver assays. In the United States and Canada the results of ore assays are reported in troy ounces per ton of 2000 pounds avoirdupois. With the ordinary system of weights a tedious calculation would have to be made for each assay with the possible mathematical errors.

The basis of the assay-ton system is the number of troy ounces (29.166 +) in one ton of 2000 pounds avoidrupois. The assay-ton is made to weigh 29.166 grams. Then

1 ton av : 1 oz. troy : : 1 A. T. : 1 milligram

Therefore using one assay-ton of ore the weight of the silver or gold in milligrams gives immediately the assay in ounces per ton.

Calibration of Weights. The weights supplied by the makers cannot always be relied upon and even originally perfect ones are subject to changes of weight due to wear or accumulation of dirt. Therefore it behooves the assayer to occasionally check his weights and to determine the correction to be applied to the marked value. This requires the use of a standardized weight which should be carefully preserved and used for this purpose only.

The method of swings should be used and the weighing is done by deflection after the sensibility (deflection of the zero for 0.1 mg.) has been determined. First determine the position of rest, and the sensibility with no load, with 100, 250 and 500 milligram loads respectively. The sensibility should not vary much throughout this range. The method to be followed can be understood from the following examples.

Calibration of a Set of Assay Weights.

Designate each weight by its marked value in the parenthesis and when there are several of the same value note some peculiarity by which they may be designated. The weights in the set, marked in milligrams are:

(500) = a, (200) = b, (100) = c, (100′) = d, (50) = e, (20) = f, (10) = g, (10′) = h, (10″) = (5) + (2) + (2′) + (1) = i.

The weight (100) is compared with the standard 100 milligram weight and the weights are then compared among themselves by the method of swings. The letters represent the true values.

In calibrating the weights from 100 milligrams to 10 milligrams, observations should be made on the following combinations:

Left Hand Pan	Right Hand Pan
(100)	100 mg. standard
(100)	(50) + (20) + (10) + (10′) + (5) + (2) + (2′) + (1)
(50)	(20) + (10) + (10′) + (5) + (2) + (2′) + (1)
(20)	(10) + (10′)

The recorded observations are as follows:—

$$\begin{array}{lll} 100\text{ mg.} & = c & - 0.020\text{ mg.} \\ c & = e + f + g + h + i & + 0.190 \\ e & = f + g + h + i & + 0.020 \\ f & = g + h & + 0.040 \\ g & = h & + 0.015 \\ h & = i & + 0.040 \end{array}$$

Solving these equations

$$\begin{array}{ll} i = i & \\ h = i & + 0.040 \\ g = i & + 0.055 \\ f = 2i & + 0.135 \\ e = 5i & + 0.450 \\ c = 10i & + 0.870 \\ c = 100.020\text{ mg.} & \end{array}$$

From these last two values of c

$$\begin{array}{r} 10i = 99.150\text{ mg.} \\ i = 9.915\text{ mg.} \end{array}$$

Substituting this value for i in the above equations we find the following values for the other weights of the set:

Designation	Actual Weight	Correction[1] to marked value
c =	100.020	+ .020 mg.
e =	50.025	+ .025 "
f =	19.965	− .035 "
g =	9.970	− .030 "
h =	9.955	− .045 "
i =	9.915	− .085 "

The smaller weights in *i*, may be calibrated in a similar manner. The large weights (100), (200) and (500) may be standardized by a simple modification of the above.

The process is made much simpler by having a complete set of

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[1] A + correction means that the weight is heavier than the normal value.

standard weights which are very carefully handled and kept solely for standardizing purposes, and these the larger assay offices usually have.

Testing Riders. Every new rider should be tested before use as they often vary 0.01 or 0.02 milligrams from their supposed value. If too heavy, a little bit at a time may be cut off with a pair of scissors until they come down to the standard.

CHAPTER V.

CUPELLATION.

In every assay of an ore for gold and silver we endeavor to use such fluxes and to have such conditions as will give us as a resultant two products:—

1st. An alloy of lead with practically all of the gold and silver of the ore and as small amounts of other elements as possible.

2nd. A readily fusible slag containing the balance of the ore and fluxes.

The lead button is separated from the slag and then treated by a process called cupellation to separate the gold and silver from the lead. This consists of an oxidizing fusion in a porous vessel called a cupel. If the proper temperature is maintained the lead oxidizes rapidly to PbO which is partly (98.5[1] per cent) absorbed by the cupel and partly (1.5 per cent) volatilized. When carried to completion the gold and silver is left in the cupel in the form of a button.

The cupel is a shallow, porous dish made of bone-ash, Portland cement, magnesia or other refractory and non-corrosive material of spongy texture. The early assayers used cupels of wood ashes from which the soluble constituents had been leached. Agricola writing in about the year 1550 mentions ashes from burned bones. Ashes from deers' horns alone he pronounces best of all; but the use of these antedate his time and he states that assayers of his day generally make the cupels from the ashes of beech wood.

To-day it is thought that the bones of sheep are the best for cupels. These should be cleaned before burning and as little silica as possible introduced with the bones. It is important not to burn the bones at too high a temperature as this makes the ash harder and less absorbent. It is also advisable to boil the bones in water before burning them as this dissolves a great part of the organic matter which if burned with the bones yields sulphates and carbonates of the alkalies.

Properly burned sheep bones will yield an ash containing about 90% calcium phosphate, 5.65% calcium oxide, 1.0% magnesium oxide, and 3.1% calcium fluoride. Ordinary commercial bone-ash also contains more or less silica and unoxidized carbon. If more than a fraction of a per cent of silica is found in bone-ash, it is evidence that sufficient care has not been taken in cleaning the bones, and cupels

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[1] Liddell, E. & M. J. 89, pp. 1264. June 1910.

made from such bone-ash aremore likely to crack during cupellation, resulting often in the loss of small buttons. If the bone-ash shows black specks it is an indication of insufficient oxidation and the assayer should allow the cupels to stand for some time in the hot muffle with the door open before using. Carbon is an undesirable constituent of cupels as it reacts with the lead oxide formed giving off CO and CO_2 which may cause a loss of the molten alloy due to spitting.

Bone-ash for cupels should be finely ground to pass at least a 40-mesh screen and the pulverized material should consist of such a natural mixture of sizes as will give a solid cupel with enough fine material to fill interstices between coarser particles. Opinions differ as to the best size of crushing for bone-ash and this will depend no doubt upon the character of the material. Bone-ash, the screen analysis of which follows, has, however, yielded particularly good cupels.

TABLE VIII. SIZE OF BONE ASH.

Size Mesh	Size mm.	Per Cent. Weight
On 40	0.380	9 Per Cent.
Through 40 " 60	0.244	14 " "
" 60 " 100	0.145	17 " "
" 100 " 150	0.098	10 " "
" 150		50 " "

With cupels made from this bone-ash it was possible to obtain losses not exceeding 1.60 per cent using 100 mgs. of silver and 25 grams of lead, while with some other lots of bone-ash containing smaller proportions of 150 mesh material it was found impossible to keep the losses below 2.0 per cent.

Making Cupels. Cupels are made by moistening the bone-ash with from 8 to 20 per cent of water and compressing in a mold. The bone-ash and water should be thoroughly mixed by kneading, and finally it should be sifted through a 10 or 12 mesh sieve to break up the lumps. Some authorities recommend adding a little potassium carbonate, molasses or flour to the mixture, but with good bone-ash nothing but pure water need be added. The mixture should be just sufficiently moist to cohere when strongly squeezed in the hands, but not so wet as to adhere to the fingers or to the cupel mold. Twelve per cent of water by weight is about right; but the amount used will depend somewhat on the bone-ash and on the pressure used in forming the cupels. The greater the pressure the smaller the amount of water which may be used. It is better to err on the side of making the mixture a little too dry than too wet.

The cupels may be molded either by hand or machine. The hand outfit consists of a ring and die. The ring is placed on the anvil and filled with the moist bone-ash, the die is inserted and pressed down firmly. It is then struck one or more blows with a heavy hammer or mallet, turning the die after each blow: finally the cupel is ejected. The cupels are placed on a board and dried slowly in a warm place. The amount of compression is a matter of experience and no exact rule for it can be given; but it may be approached by making the cupels so hard that when removed from the mold they are scratched only with difficulty by the finger nail. One man can make about 100 cupels an hour using the hand mold and die.

Several types of cupel machines are on the market. One machine has a compound lever arrangement which gives a pressure on the cupel equal to twenty times that applied to the hand lever, and by adjusting, different degrees of compression may be obtained. These machines have interchangeable dies and rings so that different sizes of cupels may be made. The rated capacity of this machine is 200 cupels an hour. Another machine made by the same company has an automatic charging arrangement. This machine is claimed to have a capacity of 600 cupels an hour. Cupels should be uniform in hardness and it would seem that with a properly designed machine a more uniform pressure could be obtained than by the use of hammer and die. Some assayers however, still prefer hand-made cupels.

Cupels should be air dried for several days at least before use. Most assayers make them up several months in advance so as to insure complete drying. They should not be kept where fumes from parting can be absorbed by them as the CaO present will be converted into $Ca(NO_3)_2$. This compound is decomposed at the temperature of cupellation and may cause spitting of the lead button.

Cupels should not crack when heated in the muffle and should be sufficiently strong so that they will not break when handled with the tongs. Good cupels give a slight metallic ring when struck together after air-drying. It is best to heat cupels slowly in the muffle as this lessens the chance of their cracking.

A good cupel should be perfectly smooth on the inside and of the right porosity. If it is too dense, the time of cupellation is prolonged and the temperature of cupellation has to be higher, thus increasing the loss of silver. If it is too porous it is said that there is again danger of a greater loss due to the ease with which small particles of alloy can pass into the cupel. The bowl of the cupel should be made to hold a weight of lead equal to the weight of the cupel.

The shape of the cupel seems to influence the loss of precious metals. A flat, shallow one exposes a greater surface to oxidation and allows of faster cupellation, it also gives a greater surface of contact between alloy and cupel, and as far as losses are due to direct absorption of alloy, it will of course increase these. The writer using the same bone-ash and cupel machine, and changing only the shape of the cupel has found shallow cupels to give a much higher loss of silver. In doing this work it was found harder to obtain crystals of litharge with the shallow cupel without freezing, and it was very evident that a higher cupellation temperature was required for the shallow cupel. The reason for this is that in the case of the shallow cupel the molten alloy is more directly exposed to the current of air passing through the muffle and consequently a higher muffle temperature has to be maintained to prevent freezing. T. K. Rose[1] also prefers deep cupels on account of smaller losses. French found shallow cupels less satisfactory on account of sprouting.

Cupellation. The muffle is heated to a bright red and the cupels, weighing about one-third more than the buttons which are to go in them, are carefully introduced and allowed to remain for at least 10 minutes in order to expel all moisture and organic matter. During this preliminary heating the door to the muffle is ordinarily kept closed, but if the cupels contain organic matter it is left open at first and then closed for five minutes or so before the buttons are introduced.

When all is ready the buttons are placed carefully in the cupels and the muffle door again closed. If the temperature of the muffle is correct and the cupels are thoroughly heated, the lead will melt at once (326° C.) and become covered with a dark gray or black scum. This should disappear in the course of a minute or two when the buttons become bright and are said to have "opened up" or "uncovered." If the buttons are practically pure lead this scum disappears when the alloy reaches a temperature of about 850° C. When the buttons have uncovered, the door of the muffle is opened to admit a plentiful supply of air to promote oxidation of the lead, while at the same time the temperature is reduced until feather-like crystals of litharge begin to form on the cupel just above the lead. If copper, nickel, cobalt, iron, etc. are present, the temperature of uncovering and also that required for cupellation will be higher, and it may be impossible to obtain litharge crystals. When air is admitted to the muffle after the "uncovering" the lead becomes lustrous and emits fumes. The lustrous appearance is caused by the flame of burning lead. The

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[1] E. & M. J. 80 pp. 934. Nov. 1905.

vapor is that of lead oxide. After cupelling has proceeded for a few minutes, a ring may be seen around the cupel just above the surface of the metal which is caused by the absorbed litharge. If the temperature is right for cupelling this will appear to be only very dull red, if bright red, the temperature is too high. The color of the alloy itself will be much brighter than that of the absorbed litharge, as it is in fact much hotter than the cupel or surrounding air, due to the heat generated by the rapid oxidation of the lead. Next to the formation of abundant litharge crystals, the appearance of the absorbed litharge is the best indication of proper cupellation temperature.

The minimum temperature at which cupellation will proceed has been somewhat of a disputed point owing largely to a difference in conception of the process and involved conditions. At least three methods of measuring the temperature have been advanced, i.e. one experimenter held his pyrometer junction one-quarter inch above the alloy in the cupel, another placed the junction inside the cupel while a third measured the temperature of the alloy itself. According to Fulton[1] the alloy itself must be between 800 and 850° C. Litharge melts at 884° (Mostowitch), 906° (Bradford), but passes through a pasty stage before becoming liquid. It would seem that the cupel itself must be maintained above the melting point of litharge in order to allow of absorption. At any event the cupel is much hotter than the space around it in the muffle due partly to the heat generated by the oxidation of the lead and partly because resting as it does on the floor of the muffle its interior portion becomes heated by conduction through the muffle floor on which it stands. Bradford[2] found 906° C. as the minimum cupel temperature which would permit of absorption of litharge. Lodge[3] found for silver cupellation with a moderate draft the muffle temperature (taken $\frac{1}{4}$ inches above the cupels) should be between 650° and 700° C.

If the temperature is exactly right feather-like crystals of litharge form on the sides of the cupel above the lead. In cupelling for silver the temperature should be maintained so that these crystals are obtained on at least the front half of the cupel, and as the button grows smaller they should follow it down the side of the cupel leaving however a slight clear space around the button. If the temperature is getting too low for the cupel to absorb the litharge, the crystals begin to form all around and close to the lead in the cupel, and soon a pool of molten litharge is seen forming all around the annular space be-

[1] Western Chemist and Metallurgist, IV. pp. 31. Feb. 1908.
[2] Jl. Ind. & Eng. Chem. 1 pp. 181.
[3] Notes on Assaying, pp. 62.

tween the lead and the cupel. If the temperature of the cupel is not quickly raised this pool increases in size and soon entirely covers the lead and then solidifies. When this occurs the button is said to have "frozen", although the lead itself may be liquid underneath. Frozen assays should be rejected as the results obtained from them, by again bringing to a driving temperature, are usually low. If the freezing is noticed at the start it may be arrested by quickly raising the temperature of the cupel in some way, i.e., by closing the door to the muffle, opening the draft, putting a hot piece of coke in front of the cupel, etc.

Beginners have difficulty in noting the first symptoms of freezing, but all should be able to see the pool of litharge starting. This gives the appearance and effect of oil, for if the cupel is moved the button slides around as if it were greased.

Toward the end of the cupellation process the temperature must be again raised, because the alloy becomes more difficultly fusible as the proportion of silver in it increases, and in order to drive off the last of the lead a temperature of about 900° C. should be reached. The temperature should not be raised so high as to melt the crystals of litharge, for if this is done too great a loss of silver results.

As the last of the lead goes off, the button is covered with a brilliant film (play of colors) and appears to revolve. The colors disappear shortly, the button becomes dull and after a few seconds appears bright and silvery. This last phenomena is called the "brightening " As soon as this occurs the cupel should be immediately drawn from the muffle far enough to have the button solidify. As it solidifies it will "flash" or "blick," i.e., suddenly emit a flash of light due to the release of the latent heat of fusion, which raises the temperature very much for a short time.

Cupels containing large silver buttons should be drawn to the front of the muffle until they chill, and just as the button is about to solidify a very hot cupel is placed over them and allowed to stand for several minutes, after which they are slowly withdrawn from the muffle. If this precaution is not taken, the buttons may "sprout" or "spit." This is caused by the sudden escape of oxygen which is dissolved in the molten silver and expelled when the button solidifies. If the button is allowed to solidify rapidly, a crust of solid silver forms on the outside, and as the central part solidifies this crust is violently ruptured by the expelled oxygen, giving a cauliflower-like growth on the button and causing particles of silver to be thrown off. As a conseqeunce the results obtained from sprouted buttons are unreliable. Buttons containing one-third or more of gold will not sprout even if rapidly withdrawn from the muffle. Sprouting is said to be an evidence of the purity of the silver.

The silver button should appear smooth and brilliant on the upper surface, silver-white in color, and spherical or hemispherical in shape according as it is small or large. It should adhere slightly to the cupel and appear frosted on the under surface. If the button is smooth on the bottom and does not adhere to the cupel it is an indication of too low a finishing temperature and will always contain lead. If it has rootlets which extend into cracks of the cupel the results are also to be taken as unreliable, as some of the silver may be lost in the cupel.

Very rich alloys of gold and silver have a peculiar mottled appearance after cupelling begins. Oily drops of litharge appear and move about on the surface of the alloy and finally run down the side of the convex surface and are absorbed by the cupel. This appearance is characteristic and once seen is again easily recognized. It may be seen toward the end of cupellation with any alloy containing much precious metal and is an indication of the approach of the end and a reminder that the temperature should be raised to insure driving off the last of the lead.

First Exercise. Practice in Cupellation.

Procedure. Take from 0.10 to 0.20 grams of silver, but do not waste time in weighing and wrap in 25 to 30 grams of sheet lead. Prepare two or three of these and cupel one at a time in order to get familiar with the operation, and with the correct temperature. To study the end phenomena "play of colors," "brightening," "blick" etc., the same of a larger amount of silver may be used with a smaller amount of lead, say 10 grams.

Have the muffle at a bright red, be sure that the cupels are dry and then heat gradually until they are red through. Allow at least ten minutes for this. Be sure that the cupels weigh more than the lead, and that the bowl is sufficiently large to contain the melted alloy. Have a row of extra cupels in front of those which are to be used and keep them there throughout the process. Keep the door to the muffle closed and when the cupel is red throughout and heated to about 850° C. place the packet of lead and silver carefully in the cupel and close the door to the muffle so that the lead will fuse as quickly as possible. As soon as the assay begins to "drive," note the time, open the door of the muffle and lower the temperature of the cupel by pulling it forward in the muffle, checking the fire if necessary, or by placing cold scorifiers, etc. around the cupel. Continue to reduce the temperature until feather crystals of litharge are seen forming on at least the front half of the cupel. Then continue the cupellation at this temperature. Finally finish the assay at a somewhat higher heat, increasing the temperature by moving the cupel back in the muffle, by starting up the fire, or by shutting off some of the cold air supply by partly closing the door to the mufflle. If the cupels are running very cold it will be necessary to start raising the temperature some minutes before the end. The fire should be under good control at all times. As soon as the cupellation is finished remove the assay carefully from the muffle to avoid sprouting. All assayers agree that the best results are obtained by having a hot start, a cold drive, and a higher heat again at the finish.

Notes) 1. When doing a large number of cupellations at one time the buttons should be charged in order of their size, i. e., largest first, so that all may start driving together.

A skillful assayer with a large muffle can run as many as 50 cupellations at one time and obtain feather crystals on all.

2. When doing a large number of cupellations at one time the cupels are not moved about after the lead is put in but the temperature is regulated by means of the draft and firing and by the use of coolers, (cold scorifiers, cupels, crucible covers, etc.) which are put in toward the back of the furnace and replaced as soon as they become heated.

3. Bear in mind that although the temperature of the muffle may be as low as 650° or 700° C., the cupel itself should be slightly above the freezing point of litharge to allow of its being absorbed. It has been found best therefore to protect the body of the cupel itself from the draft through the muffle by placing an extra row of cupels or a low piece of fire-brick in front of the first row of cupels.

4. The cupel should be withdrawn from the muffle far enough to cause the bead to solidify as soon as the brightening has taken place otherwise a loss of silver ensues.

5. Besides gold and silver the button may contain platinum, palladium, rhodium, iridium, ruthenium, osmium, and iridosmium.

6. When gold is present in considerable amounts (33%) the buttons will not sprout even if taken directly out of the muffle.

7. Certain elements, notably platinum and tellurium, give the surface of the button a frosted appearance.

8. When the finishing temperature is too low the buttons solidify without blicking. They retain lead and have a dull appearance and sometimes show flakes of litharge on the surface.

9. Buttons which contain a large amount of platinum flatten out and will not blick. They have a steel gray color and dull surface.

10. A cupel will absorb about its own weight of litharge.

Second Exercise. Cupellation Assay of Lead Bullion.

Procedure. Weigh out carefully two or three portions of bullion of ½ A. T. each. Wrap each in 10 to 15 grams of silver free lead foil so that the whole is very compact, having each piece of lead foil of the same size and weight.

Have a good fire so that the lead will melt and start to drive without delay. Use cupels which weigh 35 grams or more and have them all in a row with an extra row in front. Drop the assays in as quickly as possible and close the door. As soon as the lead starts to drive, close the drafts and cool as soon as possible so that feather crystal of litharge form on at least the front half of the cupel. Finally open the draft and otherwise increase the temperature for the last minute or two of cupellation to drive off the last traces of lead. Have some hot cupels in the muffle and as soon as the buttons brighten, pull them forward in the muffle to chill and then put a hot cupel over them and withdraw both slowly from the muffle. All danger of sprouting is over when the inside of the cupel reaches a dull red or when the bead has become solid throughout. Remove from the furnace to the cupel tray and allow to cool. When the button is cold, detach it from the cupel with the button pliers and brush with a stiff brush to remove bone-ash, or place it on its side on a clean anvil and slightly flatten with a hammer. When free from bone-ash, weigh the bead, recording in the note book the weight of gold and silver. Then part and weigh the gold, finally report the value of gold and silver in oz. per ton.

Notes) 1. Have a sheet of clean white paper at hand and when transferring the bullion from the scale-pan to the lead foil do it over this so that in case any bullion is spilled it will be seen and recovered. Do all of the wrapping and compressing over this paper for the same reason.

2. If the assay is not compact, it may overflow the cupel while melting, or else leave small particles on the sides of the cupel, which will not come down into the main button.

Loss of Silver in Cupelling. There is always some loss in cupellation and this depends on many factors such as the nature and shape of the cupel, the temperature of cupellation, the proportion of lead to silver, the amount and character of impurities, the draft through the muffle, etc. Losses may be due to spitting, absorption of bullion by the cupel, oxidation and absorption of silver with litharge, and volatilization either alone or accompanied by other metals.

The cupel surface may be regarded as a membrane permeable to molten litharge and impermeable to lead. The more nearly the material of the cupel surface approaches this condition the lower the losses may be made. Some cupels, particularly some of magnesite, present spots of material which are permeable to lead and consequently give a high loss of silver.

The most important factor relative to cupel loss, however, is the temperature. The higher the temperature, the higher the loss, is an invariable rule. The increased loss due to higher temperature seems to be due mostly to an increased oxidation of the silver and a consequent greater absorption loss. The volatilization loss is also increased by an increase of temperature. A loss of one per cent silver is allowable and the loss usually may be kept close to this figure by taking pains to cupel with abundant crystals of litharge. By overlooking this matter a loss of 4 or 5 per cent may readily be obtained and this is of course entirely inadmissable.

The following table taken from Lodge's Assaying illustrates this point and shows the importance of cupelling at the correct temperature. The temperature was taken with a Le Chatelier pyrometer, the junction being held about $\frac{1}{4}''$ above the button.

TABLE IX. EFFECT OF TEMPERATURE ON LOSS OF SILVER IN CUPELLATION.

C. P. Silver Mgs.	Lead Grams.	Temperature Deg. Cent.	Silver Loss Per cent. [1]	Remarks.
200	10	700	1.02	Crystals of PbO all around button.
200	10	775	1.30	Crystals of PbO on cooler side of cupel.
200	10	850	1.73	No crystals.
200	10	925	3.65	" "
200	10	1000	4.88	" "

The amount of lead and silver present in any button has a marked effect on the percentage loss of silver in cupellation. Rose[2] in speaking of cupellation says "The losses of silver at first are small, so long as large quantities of base metals protect it from oxidation.—Later, when the percentage of silver is high it is freely oxidized—and the oxidation is at its maximum when the silver is practically pure."

Keeping the amount of silver constant and varying the lead Lodge obtains the results shown in the following table:—

TABLE X. EFFECT OF LEAD ON LOSS OF SILVER IN CUPELLATION.

Silver Mgs.	Lead Grams.	Temperature Deg. Cent.	Silver Loss Per Cent.[3]
200	10	685	1.39
200	15	685	1.38
200	20	685	1.52
200	25	685	1.85

When the quantity of lead remains constant and the silver is varied the percentage loss of silver is found to increase as the silver is reduced. The following representative figures taken from Godshall's paper on Silver Losses in Cupellation[4] show this very clearly.

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[1] Average figures.

[2] Trans. Inst. Min. and Met. Vol. 14, p. 420.

[3] Average of two nearest together.

[4] T. A. I. M. E. 26 pp. 473–484 inc.

TABLE XI. EFFECT OF VARYING SILVER ON CUPELLATION LOSSES.

Weight of Lead	1/2 A. T.	1/2 A. T.	1/2 A. T.	1/2 A. T.	1/2. A.T.	1/2 A. T.	1/2 A. T.
" " Silver	200 Mgs.	100 Mgs.	50 Mgs.	20 Mgs.	10 Mgs.	5 Mgs.	2 Mgs.
Silver Loss	1.73%	2.03%	2.65%	2.82%	3.44%	4.46%	6.90%

Loss of Gold in Cupelling. There is always some loss of gold in cupelling but owing to its greater resistance to oxidation this loss is smaller than the corresponding silver loss. The following table taken from Lodge shows the relation between the loss of gold and the temperature of cupellation.

TABLE XIA. EFFECT OF TEMPERATURE ON LOSS OF GOLD IN CUPELLATION.

Gold Used Mgs.	Lead Grams.	Temperature Deg. Cent.	Gold Loss Per Cent.*	Remarks
200	10	700		Button Froze.
200	10	775	0.155	
200	10	850	0.385	
200	10	925	0.460	
200	10	1000	1.435	
200	10	1075	2.990	

*Mean of two results nearest together.

In the case of the gold with temperatures of 1000 degrees and above the higher losses seem to be chiefly due to a lessening of the surface tension owing to the increased temperature—for on examining the cupels with the microscope a large number of minute buttons were found all over the inner surface. It would appear that small particles of the alloy were left behind to cupel by themselves.

As in the case of silver the percentage loss of gold is found to increase as the quantity is reduced. Hillebrand and Allen [2] show that contrary to the usual opinion, the loss of gold in cupelling is not negligible, and is greatly influenced by slight changes in temperatur- They found the most exact results to be obtained when feather crystals of litharge were obtained on the cupels.

Effect of Silver on the Loss of Gold in Cupelling. Lodge in his "Notes on Assaying" states that the addition of silver in excess lessens the loss of gold but gives no figures. Hillebrand and Allen [3] state that the loss of gold in cupelling is greater with pure gold and alloys poor in silver than with alloys rich in silver. Smith[4]

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[2] Bull. No. 253. U. S. Geol. Survey. p. 20 et seq.

[3] Op cit.

[4] The Behaviour of Tellurium in Assaying. Trans. Inst. Min. and Met 17 p. 472.

gives the following figures showing the protective action exercised by silver on gold during cupellation.

	Per Cent of Total Gold Recovered.	
	Tellurium Added	Without Tellurium
Without silver	94.9	98.2
With silver	97.0	99.5

Influence of Impurities on the Loss of Precious Metals during Cupellation. According to Rose,[1] tellurium, selenium, thallium, bismuth, molybdenum, manganese, copper, vanadium, zinc, arsenic, antimony, cadmium, iron and tin, all induce extra losses of gold and silver in cupellation and should therefore preferably be removed before that stage is reached.

Of these metals the behavior of tellurium in cupellation will be mentioned in the discussion of the assay of telluride ores. Copper is perhaps the most common impurity, and on account of the difficulty of removing it completely in scorification or crucible fusions, a knowledge of its behavior in cupelling is particularly important. Eager and Welch[2] give the following table showing the effect of copper on the loss of silver in cupellation.

TABLE XII. EFFECT OF COPPER ON SILVER LOSSES IN CUPELLATION.

No.	Silver Used grams.	Lead grams.	Temp. deg. C.	Copper Per Cent. of the Silver.	Per Cent Silver Lost.		Ratio of Lead to Copper.
					Individual	Mean	
1	.20382	10	775	5	1.00		1000 to 1
2	.20256	"	"	"	1.15		"
3	.20036	"	"	"	0.93	1.03	"
4	.20618	"	"	10	1.19		500 to 1
5	.20193	"	"	"	1.09		"
6	.20118	"	"	"	1.06	1.11	"
7	.20146	"	"	15	1.35		333 to 1
8	.20138	"	"	"	1.27		"
9	.20432	"	"	"	[3]1.15	1.31	"
10	.20282	"	"	20	[3]1.15		250 to 1
11	.20100	"	"	"	1.45		"
12	.20338	"	"	"	1.46	1.46	"
13	.20224	"	"	25	1.05		200 to 1
14	.20496	"	"	"	0.95		"
15	.20420	"	"	"	1.07	1.02	"

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[1] Jour. Chem. Met. and Min. Soc. of South Africa, Vol. 5, p. 167.

[2] Thesis, No. 225, M. I. T. Mining Department.

[3] Disregarded.

It appears with this lead ratio and temperature that an increase of copper from 5 up to 20 per cent of the silver causes a steadily increasing loss of silver. With 25 per cent of copper the loss is apparently less. This was found to be due to the retention of copper in the silver button. Comparing the results shown in this table with those shown in Table IX, where no copper was used, we find that 5 and 10 per cent of copper appears to give lower silver losses than are obtained when no copper is present. This may be due to the protective action which copper is known to exert over silver.[1]

Comparing the amounts of lead and copper in 10, 11 and 12 above, we find that the ratio of lead to copper should be at least 250 to 1 to insure the removal of the copper and at least 500 to 1 if the apparent loss of silver is not to be noticeably increased.

The effect of copper on the loss of gold is shown in the following table:—

TABLE XIII. EFFECT OF COPPER ON GOLD LOSSES IN CUPELLATION.

No	Gold Used grams	Lead grams.	Temp. deg. C.	Copper Per Cent. of the Gold.	Per Cent. Gold Lost.		Ratio of Lead to Copper.
					Individual	Mean	
1	.20181	10	775	None	0.15		
2	.20104	"	"	"	0.16	0.16	
3	.20288	"	"	5	0.18		1000 to 1
4	.20110	"	"	"	0.20		"
5	.20318	"	"	"	0.10		"
(In the following the buttons show a gain in weight.)							
6	.20102	"	"	10	-0.03		500 to 1
7	.20142	"	"	"	-0.03		"
8	.20138	"	"	"	-0.02	-0.03	"
9	.20024	"	"	15	-0.11		333 to 1
10	.20060	"	"	"	-0.26		"
11	.20048	"	"	"	-0.18	-0.18	"
12	.20100	"	"	20	-0.13		250 to 1
13	.20101	"	"	"	-0.56[2]		"
14	.20161	"	"	"	-0.20	-0.17	"
15	.20422	"	"	25	-0.29		200 to 1
16	.20296	"	"	"	-0.21		"
17	.20284	"	"	"	-0.32	-0.27	"

It appears that 5 per cent of copper with this lead ratio has no effect on the loss of gold. The gain in the weight of the gold buttons with 10 and over per cent of copper shows clearly that copper is retained by the gold under these conditions. This was also indicated by the color of the gold beads. With a higher cupellation temperature

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[1] Rose, Trans. Inst. Min. and Met., Vol. 14, p. 422.

[2] Disregarded.

the amount of copper retained would doubtless be smaller. It is interesting to note that with 10 per cent of copper the amount retained by the button approximately neutralizes the loss of the gold itself. Apparently the ratio of lead to copper should not be less than 500 to 1 if the copper is to be completely removed.

Indications of Metals Present. The behavior of the cupelling lead and the appearance of the cupel and bead during and after cupellation will often give much valuable information concerning the metals present in the bullion. Thus *pure lead* gives a lemon yellow cupel, and *bismuth* the only other metal which behaves like lead in cupelling gives an orange yellow color. *Copper* gives a green to an almost black stain depending on the amount present. If too much copper is present the button will freeze, sometimes it will go down to a small amount and then flatten out leaving a copper colored button. *Antimony* comes off in the first stages of cupellation giving dense fumes and a scoria around the top of the cupel. This scoria soon solidifies and expands in so doing. If much antimony is present the cupel will be split open by this action allowing the lead to run out into the muffle, if present in smaller amounts it may simply crack the cupel and leave a ridge of yellow scoria. *Arsenic* acts much like antimony but is not so often carried into the lead button. The scoria from arsenical lead is light yellow and the fumes are less noticeable. In cupelling buttons containing *tin* this metal is quickly oxidized forming SnO_2, which if present in sufficient quantity covers the lead with an infusible scoria and stops cupellation. If *zinc* is present it will burn giving a brilliant greenish-white flame. The oxide formed condenses on the sides of the cupel and on the lead, and if present in quantity will stop cupellation. *Aluminum* is only slowly oxidized at the temperature of cupellation and in cupelling a mixture of the two metals it remains behind floating on the lead and is finally left on the side of the cupel still in the metallic state.

Iron, *nickel*, *cobalt* and *manganese* are not easily soluble in lead, but if present in any considerable amounts give infusible scoria which float on top of the lead and interfere with the cupellation. They give no marked characteristic cupel colorings as their oxides are only slightly dissolved in the litharge or absorbed by the cupel, but usually leave a brown to black stain where the masses of scoria come in contact with the cupel. Combinations of the metals influence the colors, and copper particularly covers up all of the lighter colors.

Tellurium gives a pinkish color to the surface of the cupel most of which fades away upon cooling. If much tellurium is present it gives a frosted appearance to the bead. *Platinum* and *iridium* in small amounts act similarly. Using 200 mg. of silver and 10 grams of lead the frosting made its appearance when 40 or more mg. of tellurium were added. As little as two per cent. of platinum gives the silver bead a slightly frosted appearance and 8 or 10 per cent gives a very marked rough and frosted look. Buttons which contain a large amount of platinum flatten out when near the finishing point and refuse to drive leaving a gray, mossy appearing button which sticks to the cupel. Such buttons usually retain considerable lead. *Palladium* gives the surface of the lead a raised or embossed appearance.[1] *Ruthenium* leaves a black film on the bead and a black scum on the cupel.[1] *Osmium* behaves somewhat similarly.[1]

Molten gold beads have a beautiful green color and when pure may be cooled considerable below the true freezing point. On solidification they "flash" emitting an apple-green colored light. Small quantities of iridium, rhodium, osmium, ruthenium, and osmiridium prevent this flashing.[2]

In cupelling pure gold or silver with pure lead it is found that the cupel will be stained green in the position occupied by the button as the last of the lead was going off. The higher the temperature and consequently the higher the loss of precious metals, the larger this green area becomes. Certain brands of patent cupels give a large amount of this green stain, and whenever this is found a serious loss of silver is found to have occurred.

Testing Cupels for Absorption of Silver. An occasional test of cupels and especially of each new lot of bone-ash is desirable. Select some standard amount of lead and silver and always use the same amounts so that results may be comparable. One hundred milligrams of silver and 25 grams of lead is a convenient quantity. An interesting experiment showing the amount and distribution of the silver loss as well as the relative proportion of lead absorbed and volatilized may be performed as follows:—

Procedure. Weigh out carefully on the button balance 100 or 200 milligrams of C. P. Silver and wrap in exactly 20 grams of C. P. lead. Select a hard cupel of bone-ash or magnesia, heat to cupelling temperature, cool and weigh. The cupel should be hard enough so that there will be no loss by abrasion in handling.

Cupel carefully with feather litharge crystals. Have a hot cupel

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[1] Lodge, Notes on Assaying.

[2] A. J. Van Riemsdijk, Chem. News, Vol. 41, p. 126 and 266.

at hand to act as a cover and prevent spitting. Clean and weigh the silver bead and also weigh the cupel.

Remove the bone-ash not colored with litharge and grind the remainder of the cupel to pass a 100 mesh screen. Assay for silver. See chapter on crucible assay. Report results as indicated in the following example.

Weight of C. P. silver taken	0.20047 gms.
Weight of silver after cupellation	0.19725
Silver lost during cupellation	0.00322 = 1.61%
Weight of silver found in cupel (silver absorbed)	0.00294
Weight of silver lost by volatilization	0.00028
Per cent of lost silver absorbed	91.3
Per cent of lost silver volatilized	8.9
Weight of C. P. lead taken	20.00 gms.
Weight of cupel + PbO	58.71
Weight of cupel	38.21
Weight of PbO	20.50
Weight of lead corresponding	19.04
Per cent of lead absorbed by cupel	95.20

Retention of Base Metals. It has already been mentioned that a plus error may be incurred by the retention of lead by the silver bead. If the bead contains much lead, it will appear dull or slightly yellow due to a thin coating of litharge, the bottom where it rests against the cupel will be smooth and it will not blick. A button will occasionally blick, giving the play of colors, and the "flash" even when retaining as much as one of two per cent of lead. When the alloy contains copper, the silver bead may retain from 2 to 4 per cent of copper without showing any unusual symptoms.

These retained metals tend to compensate for the absorption loss, but are so uncertain that they cannot be counted on to do so.

Portland Cement and Magnesia Cupels. Cupels of Portland cement and calcined magnesia have found favor in some localities. The former mostly in the United States and Canada, the latter principally in England and South Africa. Portland cement cupels are made from neat cement with from 6 to 10 per cent of water, in the usual way. If properly made and handled, they do not crack, and they absorb about their own weight of litharge. The silver loss due to absorption is greater than for bone-ash. Magnesite cupels are mostly factory made. They require a higher muffle temperature than bone-ash cupels. They do not crack and absorb about two-thirds of their own weight of litharge. An especially high finishing temperature is required for magnesite cupels to insure the elimination of the last of the lead. The writer has not found them satisfactory for silver work. Some makes give high silver losses and with others it is found practically impossible to drive off the last of the lead, as shown by the cupellation of known amounts of C. P. silver.

Both of these cupels have one great advantage over bone-ash cupels in that when it is necessary to assay the cupel a much better slag may be obtained from them than from the very refractory bone-ash. Portland cement has the added advantage of cheapness.

Care of the Muffle. Litharge, being a strong base, quickly attacks the material of the muffle. When, therefore, any lead or slag is spilled in the muffle, or a fusion is found to have eaten through its container, the muffle must be quickly scraped out, and the spot well covered with bone-ash. This should be worked around and if at all sticky scraped out again and more bone-ash added.

Muffles last much longer if heated and cooled slowly. When not in use the door to the muffle should be kept closed. When through with the furnace for the day close all the drafts and the door to the muffle and open the top damper so that all parts may cool down slowly.

CHAPTER VI.

PARTING.

Parting is the separation of silver from gold by means of acid. In gold assaying nitric acid is almost exclusively used, although sulphuric acid is usually employed for parting large lots of bullion. To successfully separate silver from gold by the use of nitric acid there must be present at least three times as much silver as gold and with this ratio the alloy must be in a thin sheet and it requires a long (20 minutes) continued boiling with acid of 1.26 specific gravity to effect a separation. For parting beads from ore assays it is best to have at least six times as much silver as gold present, and for ease of manipulation we would prefer not to have a much greater ratio of silver to gold than this. For with much less silver than this a long continued boiling with acid is necessary, while with much more silver than this, special precautions have to be taken to prevent the gold from breaking up into small particles which are difficult to manage. The idea of parting is to so manipulate that the gold will if possible remain in one piece.

The nitric acid for parting must be free from hydrochloric acid and chlorine in order to have no solvent action on the gold and also because any chlorides present would precipitate insoluble silver chloride on the gold. The acid strength is of great importance and the proper strength to be used depends upon the composition of the alloy. The higher the ratio of silver in the alloy, the less the acid strength should be.

Great care is necessary in parting to avoid breaking up the gold and subsequent loss of some of the small particles, as well as to insure complete solution of the silver.

Different authorities recommend different vessels for parting but for ore assays, and especially for beginners in the art, the use of a porcelain crucible or capsule is recommended and will be described first. Parting in flasks or test tubes with the use of annealing cups will also be discussed so that either method may be used.

Parting in Porcelain Capsules. A glazed porcelain capsule $1\frac{3}{8}$ inches in diameter and 1 inch high is preferable for this work on account of its broad flat base, but a small porcelain crucible does very well if care is taken not to upset it. Many different strengths of acid and other details of manipulation have been recommended but the procedure given below is one which has given uniformly satisfactory results to the author in his laboratory. The strength of acid which may be used depends on the proportion of gold and silver in the alloy, the less the ratio of silver to gold, the stronger the acid may be without danger of breaking up the gold. It is not intended that the method to be described must necessarily be followed in every case, but is designed for the safe treatment of buttons having almost any proportion of silver to gold, from 3 to 1000 or more parts of silver to one of gold.

Procedure.—Pour into the capsule about ½ inch of dilute nitric acid of 1.06 sp. gr. made by diluting 1.42 acid with seven times its volume of water. Put on the hot plate and heat until vapor can be seen rising from it and then drop in the bead which should be free from adhering bone-ash. In case the alloy has only 3 or 4 parts of silver to one of gold it must be hammered or rolled out to the thickness of an ordinary visiting card, say to 0.01 inch. The bead should begin to dissolve at once giving off bubbles of nitrogen oxides. If it does not begin to dissolve, add nitric acid 1.26 sp. gr. a few drops at a time until action starts. The solution should be kept hot but not boiling. The action should be of moderate intensity. Continue the heating until action ceases and then decant the solution into a clean white evaporating dish in a good light, taking care not to pour off any of the gold. Then add a few cubic centimeters of 1.26 sp. gr. acid, made by diluting strong nitric acid 1.42 sp. gr. with ⅓ its volume of water, and heat almost to boiling (90° C.) for from two to ten minutes. Decant this solution and then wash three times with warm distilled water, decanting as completely as possible after each washing. Apply the stream of water from the wash bottle tangentially to the sides of the capsule, rotating it meanwhile to prevent direct impact of the stream on the gold. After the final washing manipulate the particles of gold so as to bring them together, decant off the last drops of water as completely as possible and set the cup in a warm plate to dry the gold, but avoid too high a temperature as the sputtering of the last drop of water would tend to break up and possibly throw out the gold. Finally "anneal" the gold by putting the cup in the muffle or over the open flame until the bottom is bright red, when the gold will change from its black amorphous condition to the true yellow color of pure gold. It is now ready to cool and weigh. To transfer the gold from the cup to the scale-pan, bring the scale-pan to the front part of the balance. Gradually invert the cup over the pan, tapping it meanwhile with a pencil, when the gold will usually slide out without difficulty. If any small particles stick to the cup they may be detached by touching them gently with the point of the forceps or a small camels hair-brush.

The gold should be pure yellow throughout and may be compared with parted gold of known purity. If it is lighter colored than pure gold it is probable that all of the silver has not been dissolved. If it is dark in spots or if the cup is stained, it indicates incomplete removal of the silver nitrate. The "annealing" causes the gold to stick together making it easier to handle, tends to burn out any specks of organic matter which may have fallen into the cup, allows us to observe the color of the parted gold and to determine its purity in that way and to distinguish and separate any specks of foreign matter such as fire brick, coke dust etc. which may have found their way into the cup. The "annealing" at a red heat is also necessary in order that the gold may contract and lose most of its porosity, since otherwise it would condense a considerable quantity of gas during weighing.

After the silver has been dissolved from a doré alloy by the acid, the gold remains as a porous mass which is more compact the larger the proportion of gold the alloy contained, the thicker the alloy and the less the mechanical disturbance of the bead during solution. In treating a bead which is near the limiting ratio of silver to gold it is sometimes difficult to determine whether or not it is parted. This may be ascertained by touching it with a glass rod drawn down to a rather small diameter, (approximately 1/32 inch). If it feels soft throughout and can be broken up it is practically parted but it should be heated almost to boiling with 1.26 sp. gr. acid for at least ten minutes to insure dissolving the last of the silver. Such a mass of parted gold will require a longer and more careful washing, for on account of its density a longer time is required for the silver nitrate to diffuse through its minute pores. In parting the ordinary bead containing 10, 20 or more times as much silver as gold, it is easily seen when parting is complete by the considerable shrinking of the mass.

Inquartation. When the bead contains too little silver to part (less than three parts of silver to one of gold), it is necessary to alloy it with more silver in order to get the gold in a pure state. To do this, wash and dry the bead and wrap it up in say six times its weight of silver and fuse it on a piece of charcoal by means of a blow pipe, or better wrap the whole in 4 or 5 grams of sheet lead and cupel.

The term inquartation originated from the custom of the old assayers of adding three-quarters of silver to one-quarter of gold.

Many assayers when working for both gold and silver and suspecting an ore to be deficient in silver, add silver to the crucible or to the lead button before cupelling, part directly and then run separate scorification assays to determine the silver in the ore.

Preparing Large Beads for Parting: Large beads especially those which approach the maximum ratio of 25 per cent gold must be flattened on an anvil and rolled out to a thickness of about 0.01 inch before parting. During this process the alloy will require frequent annealing to prevent it from cracking. It should finally be rolled up into a little "cornet" before parting. (See assay of gold bullion.)

Notes: 1. The nitric acid solution should be hot before dropping in the bead as in cold acid the gold tends to break up into extremely fine particles.

2. The violent mechanical disturbance due to boiling or to too rapid solution may cause the gold to break up causing difficulty or actual loss in washing and subsequent handling.

3. If there remains only a few tenths of a milligram of porous gold the 10 minutes heating with 1.26 sp. gr. acid is unnecessary.

4. Strong nitric acid (1.46 sp. gr.) should not be used at any time as gold is slightly dissolved by it.

5. If in doubt at any time as to the purity of your parted gold, wrap it up in six times its weight of silver foil and carefully cupel with lead, finally re-part and weigh.

6. If a small particle of gold is seen floating on the surface of the liquid, it may be made to sink by touching it with a glass rod.

7. The black stain occurring in parting cups after heating is due to metallic silver reduced from silver nitrate by the heat, showing insufficient washing.

Parting in Flasks etc. Parting in flasks, test tubes, etc. is, up to the completion of the washing of the gold, exactly similar to that in porcelain capsules. From this point on, however, the manipulations are different, as the annealing is not done in the same vessel, but in an annealing cup. The annealing cup is a small unglazed crucible made of fire clay and very smooth on the inside.

Procedure:—After washing the gold, fill the flask or test tube with distilled water, invert over it an annealing cup and then quickly invert the two so that the gold may fall into the cup. This operation should be done in a good light and preferably against a white background. Tap the flask if necessary to dislodge any gold which has caught on the side and after all the gold has settled, raise the flask slowly until its lip is level with the top of the annealing cup. Now when all the gold is at the bottom of the cup, slip the flask quickly from the cup and invert it. Drain the water from the cup, cover it and set it on the hot plate to dry. When fully dry, it is ready to anneal and weigh. Examine the flask once more to make sure that no gold has been left in it.

This method of parting has the advantage that the acid may be boiled if necessary with less danger of its boiling over and causing loss of fine gold. It is well suited for the parting of large beads where the porcelain cup would not contain enough acid to dissolve all of the silver, and also to the parting of alloys where the ratio of silver to gold is only 2 or 3 to one and which would therefore require a long continued heating at or near boiling temperature. The methods is therefore recommended for use in the assay of gold bullion. The clay cups have the advantage of porosity so that they can absorb the last drops of water and give it off again slowly, thus preventing spattering if they are set on a hot iron plate to dry. They also stand sudden changes of temperature somewhat better than the glazed porcelain cups.

This method has the disadvantage that if all the parted gold does not remain in one piece, there is greater danger of loss because the fine gold settles with difficulty and because it cannot be watched so well through all stages of the process. There is also danger of small particles of the cup and especially the cover being broken off and mixed with the gold.

CHAPTER VII.

THE SCORIFICATION ASSAY.

The scorification assay is the simplest method for the determination of gold and silver in ores and furnace products. It consists simply of an oxidizing muffle fusion of the ore with granulated lead and borax glass. The lead oxide formed combines with the silica of the ore and also to a certain extent dissolves the oxides of the other metals. The only reagents used other than lead are borax glass and occasionally powdered silica, which aid in the slagging of the basic oxides.

The scorifier is a shallow, circular fire-clay dish 2 or 3 inches in diameter. The sizes most commonly used are $2\frac{1}{2}$, $2\frac{3}{4}$ and 3 inches in diameter.

The amount of ore used varies from 0.05 A. T. to 0.25 A. T., the amount most commonly used being 0.10 A. T. With this is used from 30 to 70 grams of test lead and from 1 to 5 grams of borax glass, depending on the amount of base metal impurities present. With nearly pure galena, or a mixture of galena and silica, a charge of 30 to 35 grams test lead and 1 gram of borax glass will suffice for 0.10 A. T. of ore, but when the ore contains nickel, copper, cobalt, arsenic, antimony, zinc, iron, tin etc. a larger and larger amount of lead and borax glass must be used dependent upon the relative slagability of the metals and the solubility of their oxides in the slags formed. Of the above, nickel and copper especially are very difficultly oxidized and when much of these are present in the ore the lead button from the first scorification will have to be rescorified once or twice with added lead. Iron, on the other hand is comparatively readily oxidized, and aside from adding an extra amount of lead and borax glass to make a fluid, slag the ore is as readily assayed as galena. Lime, zinc and antimony especially require large amounts of borax glass to convert their refractory oxides into a fusible slag.

Solubility of Metallic Oxides in Litharge. Litharge, although a strong base has the power of holding in igneous solution certain quantities of other metallic oxides. This has an important bearing on the ease or difficulty with which various metals may be slagged in scorification. According to Berthier and Percy the solubilities of the various metallic oxides in litharge are as shown in the following table:

One part of	Cu_2O	CuO	ZnO	Fe_2O_3	MnO	SnO_2	TiO_2
Requires parts of PbO	1.5	1.8	8	10	10	12	8

Antimony trioxide (Sb_2O_3) dissolves in litharge in all proportions.

Heat of Formation of Metal Oxides. Another important factor having to do with the elimination of impurities by scorification is the relative heat of formation of the various metal oxides. Having a mixture of various metal sulphides and assuming for a moment the ignition temperature to be the same for all, that reaction in which is evolved the greatest amount of heat would naturally proceed at the fastest rate. The heat of combination of various metals each with 16 grams of oxygen is shown in the following table. This basis being used on the assumption that the amount of oxygen is limited.

TABLE XIV. HEAT OF FORMATION OF METALLIC OXIDES.

Reaction.	Heat of Comb. with 16gO.	Reaction.	Heat of Comb. with 16gO.
Zinc to ZuO	870	Bismuth to Bi_2O_3	$\frac{1378}{3} = 459$
Tin to SnO_2	$\frac{1378}{2} = 689$	Copper to CuO	371
Iron to FeO	657	Sulphur to SO_2	$\frac{692}{2} = 346$
Cobalt to CoO	638	Tellurium to TeO_2	$\frac{386}{2} = 193$
Nickel to NiO	579	Silver to Ag_2O	70
Lead to PbO	503	Gold to Au_2O_3	$\frac{-158}{3} = -38$
Antimony to Sb_2O_5	$\frac{2312}{5} = 462$		
Arsenic to As_2O_5	$\frac{2194}{5} = 439$		

Ignition Temperature of Metallic Sulphides. The ignition temperature of the metallic sulphides may also be used as an indication of the order in which the various metals will be eliminated in scorification.

TABLE XV. IGNITION TEMPERATURES OF METALLIC SULPHIDES WHEN HEATED IN AIR.

Material	Formula	Ignition Temp.° C.	Material	Formula	Ignitoin Temp.° C.
Stibnite	Sb_2O_3	290–340	Galena [1]	PbS	554–847
Pyrite	FeS_2	325–427	Millerite	NiS	573–616
Pyrrhotite	Fe_xS_{x+1}	430–590	Argentite	Ag_2S	605–873
Chalcocite	Cu_2S	430–679	Sphalerite	ZnS	647–810

Nickel is by far the hardest metal to eliminate in scorification and none of the above figures exactly explain this. It is very much harder to slag than either copper or cobalt.

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[1] In Oxygen.

Notes. 1. Litharge being a strong base has a great affinity for the silica of the scorifier and especially when mixed with copper oxide it attacks it readily. When scorifying matte and copper bullion it is often necessary to add powdered silica to the charge to prevent a hole being eaten through the scorifier.

2. Some assayers add litharge to the scorification charge especially with pyritic-ores. On heating, the litharge is reduced to metallic lead, the sulphur of the pyrite being oxidized.

Scorification Assay of Silver Ore.

Procedure:—Empty the bottle or envelope of ore onto a sheet of glazed paper or oil cloth and mix thoroughly by rolling.

Take three scorifiers, $2\frac{1}{2}$, $2\frac{3}{4}$, and 3 inches in diameter respectively. Weigh out on the flux balance three portions of granulated lead 35, 45, and 55 grams respectively. Divide each lot of lead approximately in halves, transfer one half of each to the corresponding scorifier and reserve the remaining portions. Weigh out three portions of exactly 0.1 A. T. of ore on the pulp balance and place on top of the lead in the scorifiers. Mix thoroughly with the spatula and cover with the remaining portions of lead. Scatter one or two grams of borax glass on top of the lead. The scorifiers are now ready for the muffle, which should be *bright* red or yellow before the charges are put in and this temperature should be maintained during the roasting period.

Fusion Period. Place the scorifiers well back in the muffle, close the door and allow the contents to become thoroughly fused.

Roasting Period. When thoroughly fused, open the door to admit air to oxidize the ore and lead. If the ore contains sulphides these will now be seen floating on the top of the molten lead. The sulphur from these is burned going off as SO_2 and the base metals are oxidized and slagged. The precious metals remain unoxidized and are taken up by the lead bath. These patches of ore grow smaller and soon disappear, after which the surface of the melt becomes smooth, consisting of a bath of molten lead surrounded by a ring of slag.

The vapor rising from the assays will often indicate the character of the ore. Sulphur gives clear gray fumes, arsenic grayish white and antimony reddish. Zinc vapor is blackish and the zinc itself may be seen burning with a bright white flame.

Scorification Period. The lead continues to oxidize and the ring of slag around the circumference of the scorifier becomes larger as more of the lead is oxidized. Finally the whole of the lead is covered with slag and the scorification is finished. The ore should be completely decomposed and practically all of the gold and silver should be alloyed with the metallic lead.

Liquifaction Period. Close the door of the muffle and increase the heat for a few minutes to make the slag thoroughly liquid and to insure a clean pour. Then pour the contents of the scorifiers into a dry, warm, scorifier mold which has been previously coated with chalk or iron oxide. Pour carefully into the center of the mold or else the lead is likely to spatter and may not all come together in one piece. The inside surface of the scorifiers should be smooth and glassy showing no lumps of ore or undecomposed material.

When cold, separate the lead from the slag, hammer into the form of a cube and weigh to the nearest gram on the flux balance. Examine the slag and sides of the mold carefully for shots of lead and if any are found add them to the main button.

If the lead is soft and malleable, and the color of the scorifier does not indicate the presence of large amounts of copper, nickel or cobalt, the button is ready for cupellation. If it is hard or brittle it may contain impurities which must be removed by rescorifying with an additional amount of granulated lead.

Finally cupel and weigh the resultant silver or doré beads. Report in your notes the weight of ore and reagents used, the weight of lead button obtained as well as the weight and assay in oz. per ton of gold and silver. Note also the time of scorification and cupellation and describe the appearance of the scorifier and cupel.

Notes. 1. The ore must be so fine that a sample of 1/10 A..T. of it can be taken which will truly represent the whole; 100 mesh may be fine enough for some ores, 170 mesh may be necessary for some others.

2. In weighing out the ore, spread the sample which has been thoroughly mixed, into a thin sheet on the glazed paper at one side of the pulp balance. Place the weight on the right-hand pan and the ore on the left-hand pan. With the spatula mark the ore off into squares 1 inch or so on a side and then take a small portion from every square for the sample, being sure to take a section from top to bottom of the ore. During this first sampling the scale-pan should be held over the paper in one hand and the spatula in the other. When what is judged to be the right amount of ore is obtained the pan is put back on the balance and the hand with which it was held is used to turn the balance key.

The balance should be turned out of action each time ore is put on or taken off the scale-pan and the pointer need move only 1 or 2 divisions to indicate whether too much or too little ore is on the pan. To obtain the final balance, have a little too much ore in the pan, take off enough on the point of the spatule so that the condition of balance is reversed. With the balance key lift the beam only sufficient to allow the pointer to swing one or two divisions to the left of the center and then hold the key in this position. Hold the spatula over the pan and by tapping it gently with the first finger allow the ore to slide off onto the scale-pan a few grains at a time, until the balance is restored and the needle swings over to the center. By repeating this process, rejecting the ore retained on the spatula each time, an exact weight can soon be obtained.

3. If the contents of the scorifiers do not become thoroughly liquid and show a smooth surface of slag after 10 or 15 minutes, the assays require either more heat, more borax glass or more lead.

4. The lead button should weigh from 12 to 20 grams. If it is much smaller than this there is danger of a loss of silver due to oxidation, especially when the ore is rich. If the button is too large it may be rescorified in a new scorifier to the size desired.

5. The size of scorifier to be used depends upon the amount of ore, lead, borax glass and silica used, and should be such as to give a button of approximately 15 to

18 grams. If a large scorifier is used with a small amount of lead the resulting lead button will be very small and a high loss of silver will result. Again, the larger the amount of borax glass that is used the more slag there will be and the sooner the lead will be covered over.

6. Hard buttons may be due to copper, antimony or in fact almost any metal alloyed with the lead. Brittle buttons may be due to one of many alloyed metals, or to the presence of sulphur or lead oxide.

7. Ores containing pyrite require a higher temperature during the roasting period than those containing galena.

8. The white patches occasionally found in the slag are made up mostly of lead sulphate which is formed when the scorification temperature is low.

9. Instead of weighing the granulated lead, it may be measured with sufficient accuracy by the use of a shot measure or small crucible. The borax glass may also be measured.

Chemical Reactions in Scorification.

Simple Oxidation. At first, after the lead is melted and the air is admitted to the muffle, the lead begins to oxidize to PbO and this oxidation continues through the whole scorification period.

Roasting Reactions. The sulphides in the ore are roasted as indicated by the following reactions:—

$$PbS + 3O = PbO + SO_2$$
$$2PbS + 7O = PbO + PbSO_4 + SO_2$$
$$ZnS + 3O = ZnO + SO_2$$
$$Sb_2S_3 + 9O = Sb_2O_3 + 3SO_2$$

Iron pyrite breaks up on heating as follows:—

$$FeS_2 + \text{heat} = FeS + S$$

after which the sulphur is oxidized and the iron sulphide roasts.

Slag Forming Reactions. The litharge formed combines with the siliceous gangue of the ore forming silicates. The borax also combines with the various metal oxides forming borates:—

$$4PbO + SiO_2 = Pb_4SiO_6 \qquad \text{sub-silicate}$$
$$FeO + Na_2B_4O_7 = Na_2FeB_4O_8$$

Reactions Between Sulphides and Oxides. After enough PbO has been formed to slag the siliceous gangue, the litharge which is formed reacts on the partially decomposed sulphides aiding in the elimination of sulphur, thus:

$$PbS + 2PbO = 3Pb + SO_2$$
$$ZnS + 3PbO = 3Pb. + ZnO + SO_2$$
$$Ag_2S + 2PbO = 2Pb.Ag + SO_2$$
$$As_2S_3 + 9PbO = As_2O_3 + 3SO_2 + 9Pb$$

Part of the arsenic volatilizes and part goes into the slag.

If Cu_2S were present in the ore, part of it would be oxidized to CuO and then the cuprous sulphide and the cupric oxide would tend to react as follows:

$$Cu_2S + 2CuO = 4Cu + SO_2$$

A similar reaction between the litharge and the cuprous sulphide would probably take place as follows:

$$Cu_2S + 2PbO = 2CuPb + SO_2$$

The copper thus reduced and alloyed with the lead requires a prolonged scorification to remove. The two last reactions are more pronounced at high temperatures, so that for the elimination of copper in the scorification assay it is evident that a low muffle temperature should be maintained.

The color of the thin coating of slag on the scorifier is an indication of the amount and kind of metal originally present in the ore, and taken in connection with the mineralogical examination of the ore it gives a very good approximation as to its composition.

Copper gives a light or dark green depending on the amount present. If there is much iron in the ore this color may be wholly or in part obscured by the black of the iron oxide. The iron is practically wholly removed in the first scorification so that in assaying a copper matte the first scorifier may appear black while the second one will be green. The green color is said to be due to a mixture of blue cupric silicate and yellow lead silicate.

Iron. A large amount of iron makes the scorifier black, from which the color ranges from a deep red through various shades of brown to a yellow brown.

Lead in the absence of other metals makes the scorifier lemon-yellow to a very pale yellow.

Cobalt gives a beautiful blue if other metals do not interfere.

Nickel colors the scorifier brown to black depending on the amount present. When much nickel is present the cupel becomes covered with a thick film of green nickel oxide.

Manganese colors the scorifier brownish black to a beautiful wine color.

Arsenic and *antimony* if present in large amount, will leave crusts on the inner surface of the scorifier even if much borax glass is used.[1] In the absence of other metals these scoria will be yellow in color.

If a scorifier is colored dark green, indicating much copper, dark blue, indicating much cobalt, or black with infusible scoria, indicating nickel the button should be scorified again with more lead.

Rescorifying Buttons: When rescorifying to remove copper or other impurities, add sufficient lead to bring the total amount of lead up to 50 grams and scorify at a low temperature using a 3″ scorifier. Place the scorifier in the muffle, heat to scorifying temperature (to

[1] Lodge.

remove moisture) and then drop in the lead. Sometimes a button requires as many as three scorifications before it is sufficiently pure to cupel.

Buttons weighing over 30 grams should be scorified to 12 or 15 grams before being cupelled, as the loss of silver should be less by the combined method than by direct cupellation.

Spitting of Scorifiers. Occasionally small particles of lead are seen being projected out of the scorifier. This is due to decrepitation of the ore or to the action of some gas given off by the ore or scorifier itself. If the particles of lead do not all fall back into the scorifier a loss of precious metal will result. The direct cause may be found in some of the following and a proper remedy applied:

1. Dampness of scorifier.
2. Presence of carbonates in clay from which scorifier was made.
3. Imperfect mixing of charge, resulting in ore being left on the bottom of the scorifier and covered with lead.
4. Too high a temperature at the start, resulting in too rapid oxidation of sulphides, evolution of CO_2 or violent decrepitation.
5. Admittance of air into the muffle too soon, resulting in too rapid oxidation. Especially to be avoided in the case of ores or products carrying zinc.
6. Character of the ore itself. Ores containing carbonates etc. are not suited for scorification.

Assaying Granulated Lead. Almost all assay reagents contain traces of gold and silver, but the lead and litharge especially are most likely to contain these metals in appreciable amounts. Each new lot of granulated lead which is obtained should be sampled and assayed before it is used, and in case any silver or gold is found a strict account must be kept of the lead used in each assay and a correction for its precious metal contents made.

Procedure: Scorify 2 or 3 portions of 120 grams each in 3½ or 4″ scorifiers. If necessary rescorify until the buttons are reduced to 15 or 20 grams. Cupel, weigh and part. This correction must be made even if extremely small, as any error thus introduced would be multiplied by 10 in reporting the results in oz. per ton.

Scorification Assay for Gold. The silver in an ore can be determined with a sufficient degree of accuracy by taking 1/10 A. T. for each assay, since we may thus determine the contents of the ore to 1/10 of an ounce, or its value to 5 or 6 cents a ton. When however we determine gold to 1/10 of an ounce per ton by this same method, we have determined its value to only $2.00 per ton, which is not sufficiently accurate for any but very high grade ores. For this reason the scorification assay is not usually chosen for gold ores unless they contain impurities which interfere decidedly with the crucible assay. (See scorification assay of copper matte and bullion.)

Scorification Assay of Copper Matte.

Procedure: Take three portions of 1/10 A. T. of matte, and mix with 30 grams of granulated lead and 1 gram powdered silica in a 3-inch scorifier and cover with 30 grams more of lead. Put ½ gram of borax glass on top. Scorify hot at first and then at a low temperature to facilitate slagging the copper.

When the lead eye covers, pour as usual and separate the lead from the slag. Weigh each button and add sufficient granulated lead to bring the total weight to 50 grams and drop into three new scorifiers which have been heated in the muffle. Add about 1 gram of silica and scorify at a low temperature.

Repeat this second scorification if necessary until the cool scorifiers are light green. Cupel as usual. The color of the cupel should be greenish and not black. The latter color indicates insufficient scorification.

Weigh the combined silver and gold and part, weighing the gold.

See special methods of assay for details of this and other methods of assay of copper-bearing material.

Notes. 1. For matte containing not more than 30 per cent of copper two scorifications are sufficient.

2. This method gives rather high slag and cupel losses and for exact work the slags and cupels are re-assayed and a correction made for their silver and gold contents.

3. The final silver beads will often contain from 2 to 4 per cent of copper.

4. When accurate results in gold are desired as many as 10 portions of 1/10 A. T. each of matte are scorified and the buttons combined for parting and weighing.

The scorification process is particularly suited to sulphides, arsenides and antimonides of the difficultly oxidizable base metals, particularly nickel, copper and cobalt. It is used in many localities for the silver in all sulphide ores, as well as for copper and nickel mattes. When gold is to be determined some other method is generally used. The scorification assay is not commonly used for the assay of siliceous ores.

The following changes have been found generally satisfactory:—

TABLE XVI. SCORIFICATION CHARGES FOR DIFFERENT ORES.

Ore	Charge				Scorifier	Heat High at First then
	Ore A. T.	Granulated Lead gms.	Borax Glass gms.	Silica gms.		
Galena	0.1	35	½–1	–	2¼″	Low
½ Galena ½ Silica	0.1	35	½–1	–	2¼″	Low
Low grade galena	0.2	45	½–1	–	2½″	Low
Pyrite	0.1	50	2–3	–	2¾″	Medium
½ Pyrite ½ Silica	0.1	45	1–2	–	2½″	Medium
Stibnite	0.1	50–60	1–2	–	2¾–3″	High
Sphalerite	0.1	60	3–5	1–2	3″	High
Arsenical ores	0.1	45–60	1–2	–	2¾–3″	High
Cobalt ore	0.1	60	3	–	3″	High
Nickel ore	0.05–0.1	60	3	–	3″	High
Chalcopyrite	0.1	60	1–2	1	3″	Low
Tin ores	0.1	60–70	2–3	1	3–3½″	High
Lead matte	0.1	50	½	–	2¾″	Low
Copper matte	0.1	60	1	1	3″	Low

Losses in Scorification. Losses in scorification may be due to "spitting," volatilization, oxidation and slagging as well as losses of shots of alloy. Some loss due to oxidation and slagging is unavoidable, but it should be low. If there is any decided loss by volatilization it shows that the process is unsuited to the ore.

The tendency of scorification assays to "spit" is one of the most serious objections to the process. Ores which decrepitate or contain volatile constituents such as CO_2, H_2O, etc. ($CaCO_3$, $CaSO_4 2H_2O$) are unsuited to the process and should be assayed by crucible methods. Very often a preliminary glazing of the scorifier with a mixture of sodium carbonate and borax-glass will prevent spitting. The scorifiers should always be kept in a warm, dry place.

Losses of alloy due to failure of all the lead to collect in one piece may be due to careless pouring, by which some of the lead may splash on the side of the mold and solidify there, or on account of poor slag, or a cold pour, some shots of alloy may be left in the scorifier or scattered through the slag in the mold.

As scorification is an oxidizing process it is only reasonable to expect some loss due to oxidation of the precious metals, and this will naturally be greater the longer the scorification is continued and the more intense the oxidizing action. Silver is more easily oxidized than gold, therefore we should expect a much greater loss of silver than of gold. To keep this loss at a minimum let the liquifaction period be thorough. The molten lead tends to reduce and collect some of the silver previously slagged. Some assayers recommend sprinkling a small amount (about 0.2 grams) of charcoal over the slag in the scorifier just before pouring, with the idea of reducing some lead from the slag and thus collecting most of the oxidized silver by the rain of lead shot thus induced. English authorities almost invariably recommend this practice which they term "cleaning the slag."

CHAPTER VIII.

THE CRUCIBLE ASSAY.

Theory of the Crucible Assay. The majority of ores are infusible, or nearly so, by themselves, but if pulverized and mixed with suitable reagents in proper proportion the mass will readily fuse at an easily attained temperature. The finer the ore is crushed, the better and more uniform are the results usually obtained. We assume in considering a crucible assay that there is such a thorough mixture of ore and fluxes that each particle of ore is in contact with one or more particles of litharge and reducing agent. As the temperature of the mass is gradually raised, part of the litharge is reduced to lead (commencing at 500° to 550° C.) by the carbon of the charge and these reduced shots of lead, alloy and take up the gold and silver from the surrounding particles of ore, so far at least as the precious metals are free to alloy.

At about this same temperature, 560° C., the borax of the charge begins to melt and to form fusible compounds with some of the bases of the flux and ore charge. At 625° C. lead oxide and silica commence to combine and from this point the slag begins to form rapidly. The conditions should be such that the slag remains viscous until the ore particles are thoroughly decomposed and every particle of gold and silver has been taken up by the adjacent suspended globules of lead. After this point has been passed, the temperature may be raised until the slag is thoroughly fluid, when the lead particles combine and falling through the slag form a button in the bottom of the crucible in which practically all of the precious metals originally present in the ore are concentrated.

To make an intelligent crucible assay it is necessary to know the mineral character of the ore, for a siliceous ore requires a different treatment from one which is mostly limestone and a sulphide requires to be treated differently from an oxide. For the purpose of the assayer, ores should be considered from two standpoints, first according to the character and quantity of their slag forming constituents, and second according as they are oxidizing, neutral or reducing in the crucible fusion with lead and lead oxide.

Ores Classified According to Slag Forming Constituents. The principal slag forming constituents of ores and gangue minerals arranged approximately in the order of their occurrence in the earth's crust are as follows:—

Silica	SiO_2	Acid
Alumina	Al_2O_3	Bases
Ferrous-oxide	FeO	
Manganous-oxide	MnO	
Calcium-oxide	CaO	
Magnesium oxide	MgO	
Sodium oxide	Na_2O	
Potassium oxide	K_2O	
Zinc oxide	ZnO	
Lead oxide-	PbO	
Cuprous oxide	Cu_2O	

These oxides with the exception of those of sodium, potassium and lead are infusible at the temperature of the assay furnace. To get them into the molten condition we add fluxes. According to Percy, "a flux is something which if added to a substance infusible or difficultly fusible by itself will cause it to fuse."

All of the common assay fluxes with the exception of silica are readily fusible by themselves. In general it may be said that to flux the acid, silica, it is necessary to add bases, and to flux any of the basic oxides acids must be added. To flux alumina it is best to add both acids and bases, thus making what is termed a double silicate.

Ores Classified According to Oxidizing or Reducing Character. According to their oxidizing or reducing character in the crucible assay ores may be divided into three classes as follows:

Class 1. *Neutral Ores.* Siliceous, oxide and carbonate ores or ores containing no sulphides, arsenides, antimonides, tellurides, etc., i.e. ores having no reducing or oxidizing power.

Class 2. *Ores Having a Reducing Power.* Ores containing sulphides, arsenides, antimonides, tellurides etc. or containing carbonaceous matter, or ores which decompose litharge with a reduction of lead in the crucible fusion.

Class 3. *Ores Having an Oxidizing Power.* Ores containing ferric oxide, manganese dioxide etc. or ores which when fused with fluxes oxidize lead or reducing agents. Ores with any considerable oxidizing power are comparatively rare.

Determining the Character of a Sample. The mineral character of an ore can be most readily determined when the ore is in the coarse condition. As however a large proportion of the samples received by the assayer are already pulverized, it becomes necessary for him to be able to form a close estimate of their composition in this condition. This may be best accomplished by washing a small sample on a vanning placque or shovel.

Vanning. Place one or two grams of the ore on the vanning shovel, cover it with water and allow it to stand until the ore is thoroughly wet, shake violently in a horizontal plane until the fine slimes are in suspension and all lumps are broken up. Allow it to settle a moment, decant some of the water if necessary and then separate the ore according to the specific gravity of its different minerals by a combined washing and shaking. The water should be made to flow over the ore in one direction only and the velocity of the shaking motion should be accelerated in a direction opposite to the flow of the water. The shaking tends to stratify the ore, heaviest next the pan, lightest on top, while the water tends to wash everything downward, the material on top most because of its position, and also because of its lesser specific gravity. Finally if there are a number of minerals present, they should appear spread out in fan shape in order of their specific gravity, for instance, galena, pyrite, sphalerite and quartz.

Crucible Slags. The slags obtained in the crucible assay may be regarded as silicates and borates of the metallic oxides. The acid constituents of rocks other than silica so seldom play an important part in the formation of slags that they may be omitted at least from a preliminary discussion of the subject.

A slag suitable for assay purposes should have the following properties:—

1. A comparatively low formation temperature readily attainable in assay furnaces.

2. It should be pasty at and near its formation temperature, to hold up the particles of reduced lead until the precious metals are liberated from their mechanical or chemical bonds and are free to alloy with the lead.

3. It should be thin and fluid when heated somewhat above its melting point, so that shots of lead may settle through it readily.

4. It should have a low capacity for gold and silver, and should allow a complete decomposition of the ore by the fluxes.

5. It should not attack the material of the crucible too violently.

6. Its specific gravity should be low, to allow of a good separation of lead and slag.

7. When cold, it should separate readily from the lead.

Classification of Silicates. Silicates are classified according to the proportion of the oxygen in the acid to oxygen in the base. Thus a mono-silicate has the same amount of oxygen in the acid as in the base. A bi-silicate has twice as much oxygen in the acid as in the base and so on.

The silicates which have been found to behave satisfactorily as assay slags lie within the following limits:—

TABLE XVII. CLASSIFICATION OF SILICATES.

Name	Oxygen Ratio Acid to Base	Formula. R = Bivalent Base
Sub-silicate	½ to 1	$4RO.SiO_2$
Mono-silicate	1 to 1	$2RO.SiO_2$
Sesqui-silicate	1½ to 1	$4RO.3SiO_2$
Bi-silicate	2 to 1	$RO.SiO_2$
Tri-silicate	3 to 1	$2RO.3SiO_2$

The formation temperature and melting point of the different silicates depends not only on the relation of the silica to base, but also on the nature of the bases present. Thus we say that within the above range the silicates of lead and the alkalies are all readily fusible, the iron and manganese silicates are difficultly fusible and the silicates of calcium, magnesium and aluminum are infusible at the temperature of the assay furnace. Note that so far we are referring to the individual silicates of the different bases and not to mixtures of the same.

Of these slags the bi- and the tri-silicates have but little effect on the ordinary assay crucible while the sub-silicates attack it strongly to satisfy their desire for silica.

The student should distinguish between the formation temperature of a slag and the melting point of the same slag when already formed. It has been shown by Day,[1] that when the constituents of a slag are finely crushed and intimately mixed as in an assay fusion, the formation temperature of the slag is decidedly lower than the melting temperature. That is to say, the slag forms without melting and actually passes through a pasty stage before coming to perfect fusion.

Action of Borax in Slags. Borax ($Na_2B_4O_7 + 10H_2O$) melts at about 560° C. and gives up its water of crystallization forming borax-glass. Borax-glass when molten is decidedly viscous and on account of its excess of boracic acid it acts as an acid flux.

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[1] Journal Am. Chem. Soc. 28, p. 1039 (Sept. 1906)

To determine what relation it bears to silica as regards its acid fluxing quality we may consider the matter first from a theoretical standpoint, and then from the results of experiments.

Considering the borates from their metallurgical classification, i.e. according to the amount of oxygen in the acid to that in the base, we may compute the weight of borax-glass necessary to form a mono-borate with a unit weight of sodium carbonate and compare this with the amount of silica required to form a mono-silicate with the same amount of base. From the rational formula for borax-glass ($Na_2O.2B_2O_3$) we see that to form the mono-borate ($6Na_2O.2B_2O_3$), borax-glass requires five additional molecules of Na_2O. The equation may be written as follows:—

$$5Na_2CO_3 + Na_2O.2B_2O_3 = 6Na_2O.2B_2O_3 + 5CO_2$$

Whence we may write the following proportion to find the amount of borax-glass necessary to form a mono-borate with 100 grams of soda:—

$$5Na_2CO_3 \ : \ Na_2O.2B_2O_3 = 530 \ : \ 202 = 100 \ : \ x$$

Solving, x is found to equal 38.1. In the same way we may find the amount of silica necessary to form a mono-silicate with 100 grams sodium carbonate.

$$2Na_2CO_3 \ : \ SiO_2 = 212 \ : \ 60 = 100 \ : \ y$$

Solving, y is found to equal 28.3. Whence, from the theoretical standpoint we may say that in the case of a mono-silicate slag 38.1 gram of borax-glass is equivalent to 28.3 grams of silica, or when borax-glass is used to replace silica in a mono-silicate slag one gram has the same effect as 0.743 grams of silica.

For a bi-silicate slag the relation is different owing to the molecule of Na_2O already in the borax-glass. The amount of borax-glass required to form a bi-borate with 100 grams of sodium carbonate is 95.3 and the silica for a bi-silica is 56.6. Thus in the case of a bi-silicate slag one gram of borax-glass is equivalent to 0.584 grams of silica.

The results of experiments[1] on the size of lead buttons obtained in reducing power fusions with varying amounts of silica in some instances and borax-glass in others give results approaching the theoretical values obtained above. They show that 10 grams of borax-glass has the same effect in preventing the reduction of lead from litharge as between 6 and 7 grams of silica.

Rose[2] in a discussion of the refining of gold bullion with oxygen gas made a number of experiments to determine the best proportions of borax, silica and metallic oxides. Borax alone was found to be

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[1] Lodge Notes on Assaying, 2nd Edit. p. 86.

[2] Inst. Ming. & Metallurgy, 14 p. 396, April, 1905.

unsatisfactory on account of the rapid corrosion of the crucible. Silica alone gave a pasty, very viscous, slag. The best slag found corresponded nearly to the formula $\frac{2}{3}$ (Na_2O, B_2O_3) + 3 RO, $\frac{2}{3}$ B_2O_3, $3SiO_2$. This is made up according to the following formula, $9RO + 2Na_2B_4O_7 + 9SiO_2$, where R = Ca, Mg, Pb, Zu, Cu, $\frac{2}{3}$Fe, $\frac{2}{3}$Ni. Leaving out of account the metaborate of soda $Na_2B_2O_4$, it is a boro-silicate in which the relation of oxygen in acids to oxygen in bases is 2.66 to 1. This slag melts at a low temperature and is very fluid at between 1000° and 1100° C. It has only a slight corrosive action on clay crucibles. The flux contains 3 parts by weight of borax glass to 4 parts of silica.

Charles E. Meyer[1] in fluxing zinc box slime, made zinc into bi-silicate with silica and added $Na_2B_4O_7$ for other bases all assumed to be Fe_2O_3 pound for pound, i.e. 1 lb. $Na_2B_4O_7$ for 1 lb. Fe_2O_3.

Fluidity of Slags. It is also necessary to distinguish between the melting point and the fluidity of slags. Many slags of low melting and formation temperature are entirely unsuited for assay purposes on account of their viscous nature when melted. As a rule, the higher the temperature the more fluid a slag will become, but different slags vary much in this respect. All slags are viscous at their freezing point, yet one slag will be thinly fluid 200° C. above its melting point and another wlll be decidedly viscous at this degree of superheat. The viscosity of silicates increases with the percentage of silica above that required for the mono-silicate, and the same may be said for borates.

These silicates and the slags resulting from mixtures of them must not be thought of as chemical compounds, but rather as solutions of one thing in another, as for instance lead silicate, a solution of silica in molten litharge and vice versa. When solidified a slag may be either a glass, i.e. a solid solution, or a mixture after the nature of an alloy.

Acid and Basic Slags. Slags more acid than the mono-silicate are generally termed acid, while those approaching a sub-silicate are called basic. The acid slags are all more or less viscous when molten and can be drawn out into long threads. They cool slowly and are usually glassy and brittle when cold. The basic slags are usually extremely fluid when molten, they pour like water with no tendency to string out, in fact they may even be lumpy where the bases are in too great excess. They solidify rapidly and usually crystallize to some extent during solidification. Basic slags are dull and tough

[1] Jl. Chem. Met. & Ming. Soc. of South Africa, 5 p. 168, Jan. 1905.

when cold. They are usually of a dark color and on account of the large proportion of bases they contain they usually have a high specific gravity.

Mixed Silicates. The mixture of two or more fusible compounds usually fuses at a lower temperature than either one taken alone, just as for example a mixture of potassium and sodium carbonate fuses at a lower temperature than either one of them alone. For this reason assayers always provide for the presence of a number of easily fusible substances, although their presence is not always necessary for the decomposition of the ore. For instance, even in the assay of pure limestone, a base, a certain amount of sodium carbonate also a base is always added.

Use of Fluxes. For the sake of economy in material and time it is best to limit the amount of fluxes to the needs of the ore. The great saving to be made in this way may be illustrated as follows: If we use twice as much flux as necessary, we have to use twice as large a crucible, which cuts down the furnace capacity very considerably, and besides the large charges require a longer time in the furnace to fuse and decompose the ore.

Slags for Class 1. Siliceous Ores. To fuse a siliceous ore, basic fluxes must be added, the alkali carbonates and litharge being the ones at our disposal. The bi-silicates of soda and lead being readily fusible and sufficiently fluid for our purpose we may limit our basic fluxes to the amount necessary to form these silicates. Sodium carbonate and litharge combine with silica to form bi-silicates in proportions indicated in the following equations:—

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$$

$$PbO + SiO_2 = PbSiO_3$$

From a comparison of the molecular weights of the left hand members of these equations, it may be determined that one assay-ton of pure silica will require either 51.5 grams of sodium carbonate, or 108 grams of litharge to form a bi-silicate. As the mixed silicate of soda and lead works better than either one alone it will be wise to make a double silicate of the approximate formula $Na_2O.PbO.2SiO_2$. We may use 30 grams of soda (3 /5) and 45 grams of litharge (2 /5) for one assay-ton of silica or any other inversely proportional amounts of the two.

In assaying an ore we must also provide for a lead button to act as a collector of the precious metals. A 25 gram button is usually sufficient. To allow for this we will need to add 28 grams more of litharge (92% lead) and also some reducing agent say $2\frac{1}{4}$ grams of argols (R. P. 10).

Our charge will now stand as follows:—

Ore	1 A. T.
Sodium-carbonate	30 Grams
Litharge for slag 45 gms.	70 Grams
Litharge for button 25 gms.	
Argols (R. P. 10)	$2\frac{1}{4}$ Grams

So far we have been considering an ideal ore, pure silica. This, however, is rarely if ever found in practise. The ordinary so called siliceous ore rarely contains more than 90 per cent of silica and often not more than 80 or 85 per cent. The rest of the ore will be either neutral or basic, usually basic, such as Al_2O_3, Fe_2O_3, MnO_2, CaO, MgO, etc. or will be in the form of some sulphide mineral as pyrite, which will be converted into a base during the fusion.

To take care of these bases and still maintain a bi-silicate slag, we have the choice of two options; we may calculate how much of the silica of the ore will combine with the bases thereof, and then supply basic fluxes for the remaining silica, or we may supply basic fluxes for all of the silica and then supply acid fluxes, preferably borax or borax-glass, to form a bi-silicate or its equivalent bi-borate with the bases of the ore. This second method is the one generally followed in practice, that is to say for all siliceous ores a fixed amount of soda, borax, litharge and reducing agent is used and then if there is much iron, manganese, calcium, magnesium or aluminum oxide present an additional amount of borax is added to the charge, not usually or simply to make the slag more acid but more especially to make a better and more fusible slag with these rather refractory metal oxides.

The following are examples of bi-silicate charges for siliceous ores,

Ore	$\frac{1}{2}$ A..T.	1 A. T.	2 A. T.
Soda (Na_2CO_3)	15 gms.	30 gms.	60 gms.
Borax	3–5 “	5–10 “	10–15 “
Litharge	50 “	70 “	120 “
Argols (R. P. 10)	$2\frac{1}{4}$ “	$2\frac{1}{4}$ “	$2\frac{1}{4}$ “

The larger the amount of ore used the more necessary it becomes to keep down the quantity of fluxes. The following charges more acid than the bi-silicate are regularly used in this laboratory for the assay of siliceous tailings. If the tailings were pure silica the slags would be almost tri-silicates.

Ore	1 A. T.	2 A. T.	5 A. T.
Soda (Na_2CO_3)	30 gms.	60 gms.	150 gms.
Borax	3 "	6 "	15 "
Litharge	60 "	90 "	180 "

Argols . . for a 25 gram bead button.

The results obtained with the last mentioned charges are good, the slags of course are more viscous than the bi-silicate slags but they pour well even when fusions are made in the muffle furnace. The crucibles are practically unattacked and can be used for many such fusions if of good quality and especially if care is taken to cool them slowly.

The following table of bi-silicate factors contains all of the data necessary for fluxing siliceous ores with any of the common basic fluxes, and it is thought that the above explanation will make its use readily understood.

TABLE XVIII. BI-SILICATE SLAG FACTORS. NO. 1.

SiO_2	Quantity of Bases Required.			
	PbO	Na_2CO_3	K_2CO_3	$NaHCO_3$
1 assay-ton	108.4 gms.	51.5 gms.	67.1 gms.	81.7 gms.
10 grams	37.1 "	17.7 "	23.0 "	28.0 "

One gram of FeO neutralizes 8/10 gms. SiO_2 or requires 1.4 gms. borax-glass. One gram of $CaCO_3$ neutralizes 0.5 gms. SiO_2 or requires 1.0 gms. borax-glass.

To make a bi-silicate slag and at the same time to keep the quantity of fluxes at a minimum the procedure would be as follows:—First, find the amount of silica which will be converted into bi-silicates by the bases of the ore. Second deduce this quantity from the amount of silica in the ore and add basic fluxes for the remainder.

For example take an ore of the following composition:—SiO_2 80%, FeO 10%, $CaCO_3$ 10%, ore charge 1 assay-ton.

Silica equivalent FeO	$2.916 \times .8 =$	2.32 gms.
" " $CaCO_3$	$2.916 \times .5 =$	1.46
Total		3.78
Silica in ore	$.80 \times 29.166 =$	23.33 gms.
less silica equivalent of FeO and $CaCO_3$		3.78
Silica for which fluxes are to be added		19.55 gms.

Starting with 30 grams of soda (Na_2CO_3) and adding 10 grams of borax this gives the following charge:—

Ore	1 A. T.
Sodium-carbonate	30 gms.
Borax	10 “
Litharge for slag 23	50 “
Litharge for lead button 27	
Argols	for 25 gram button.

Following the more usual custom of adding a given amount of soda-litharge flux and then adding extra borax for the bases, we have simply to compute the borax to add for the 10 per cent of ferrous oxide and limestone.

Borax glass equivalent FeO	$2.916 \times 1.4 =$	4.08
Borax glass equivalent $CaCO_3$	$2.916 \times 1.0 =$	2.92
Total		7.00

Whence the charge becomes

Ore		1 A. T.
Soda (Na_2CO_3)		30 gms.
Borax-glass	3 + 7	10 “
Litharge		60 “
Argols		for a 25 gram lead button.

Slags for Class 1 Basic Ores. In the assay of basic ores we have to add acid fluxes, silica and borax to obtain a fusible slag. Also on account of the fact that the silicates of iron, manganese, calcium, magnesium and aluminum are by themselves infusible, or nearly so, at the temperature of the assay furnace, it is always customary to add some soda and excess litharge to the charge. These latter, combining with some of the silica and borax, form readily fusible compounds which help to take into solution the silicates of the basic oxides and by diluting them give more fusible and fluid slags. A quantity of soda equal at least to that of the ore is generally taken as a starting point, and very often a quantity of litharge equal to that of the ore is also allowed for the slag.

The silicate degree of the slag will depend on the character of the bases. For Class 1 ores consisting principally of iron, manganese, calcium, magnesium and aluminum it has been found best to approximate a sesqui or a bi-silicate slag.

The following table of bi-silicate slag factors will facilitate the calculation of charges for basic ores.

TABLE XIX. BI-SILICATE SLAG FACTORS NO. 2.

Quantity of Bases.	Quantity of Acid Required.
1 A. T. FeO	24.3 gms. SiO_2
1 A. T. $CaCO_3$	17.6 " "
1 A. T. $MgCO_3$	21.0 " "
1 A. T. MgO	43.74 " "
10 gms. PbO	2.7 " "
30 " $NaHCO_3$	10.8 " "
30 " Na_2CO_3	16.4 " "
10 " K CO_3	4.4 " "

For sesqui-silicates use three-quarters of the above quantities of silica.

When borax-glass is substituted for silica consider that one gram of borax-glass is equivalent to 6/10 gram of silica. The amount of silica which should be replaced by borax has not been determined, but on account of the greater fusibility and fluidity of boro-silicates it is well to replace at least $\frac{1}{4}$ to $\frac{1}{2}$ of the silica with its equivalent of borax or borax-glass.

The following example will illustrate the use of the table. Take an ore of the following composition $CaCO_3$ 90%, SiO_2 10%, ore charge 1 assay-ton. Starting with 30 grams of sodium carbonate and 50 grams of litharge, 20 for the slag and 30 for the lead button and planning for a bi-silicate slag the silica requirements of the different bases are as follows:—

The $CaCO_3$ of the ore requires 0.9 × 17.6	= 15.80 gms. SiO_2
30 grams soda requires	= 16.4 " "
20 " PbO "	= 5.4 " "
Total	37.6
Deducing the silica of the ore	2.9
Silica or equivalent borax necessary	34.7

Putting in say 20 grams of silica we have to provide borax equivalent to 34.7 − 20 = 14.7 grams of silica or 24 grams borax-glass.

The final charge stands

Ore	1 A. T.	Litharge	50 gms.
Sodium carbonate	30 gms.	Argols for 25 gram button	
Borax-glass	24 gms.	Silica	20 gms.

Reducing and Oxidizing. Reducing and oxidizing reactions, are common in fire assaying as in other chemical work, and practically all fusions are either reducing or oxidizing in nature. For instance, the scorification assay is an oxidizing fusion in which atmospheric air is the oxidizing agent, while the crucible fusion of a siliceous ore is a reducing fusion in which argols, flour or charcoal act as the reducing agents.

By *reducing power* as used in assaying is meant the amount of lead that one gram of the ore or substance will reduce when fused with an excess of litharge. For instance, if we use 5.00 grams of ore and obtain a lead button weighing 16.50 grams the reducing power of the ore is

$$\frac{16.50}{5.00} = 3.30$$

By *oxidizing power* is meant the amount of lead which one gram of the ore or substance will oxidize in a fusion, or more exactly it is the lead equivalent of a certain amount of reducing agent or ore which is capable of being oxidized by one gram of the ore or substance.

Reducing Reactions. The reduction of lead by charcoal is shown by the following reaction:—

$$2PbO + C = 2Pb + CO_2$$

From which it is seen that one gram of pure carbon should reduce $\frac{2 \times 207}{12} = 34.5$ grams of lead. As however charcoal is never pure carbon the results actually obtained in the laboratory will be somewhat less usually from 25 to 30. All carbonaceous materials have more or less reducing power. Those most commonly used as reducing agents in assaying are charcoal R. P. ± 27.5, argols R. P. 8–12, cream of tartar R. P. 5.5, flour R. P. 9 – 12.

Besides carbonaceous matter many other substances and elements are capable of reducing lead from its oxide. The most important of these are metallic iron, sulphur and the metallic sulphides. The reduction of lead by iron is shown by the following reaction:—

$$PbO + Fe = Pb + FeO$$

Whence the reducing power of iron is $\frac{207}{56} = 3.7$

The reducing power of sulphur and the metallic sulphides will vary, dependent on the amount of alkaline carbonate present. For instance, the reduction of lead by sulphur in the absence of alkaline carbonates is shown by the following reaction:—

$$2PbO + S = 2Pb + SO_2$$

The reducing power of sulphur under these conditions would be

$$\frac{2 \times 207}{32} = 13$$

In the presence of sufficient alkaline carbonates the sulphur is oxidized to sulphur-trioxide which combines with the alkali to form a sulphate. The reaction is as follows:—

$$3PbO + S + Na_2CO_3 = 3Pb + Na_2SO_4 + CO_2$$

From which we see the reducing power of sulphur under these conditions should be

$$\frac{621}{32} = 19.4$$

In the same way we find that the reducing power of the metallic sulphides varies according to the amount of available alkaline carbonate present. For instance, in the absence of alkaline carbonates the following equation expresses the reaction between iron pyrite and litharge:—

$$FeS_2 + 5PbO = FeO + 5Pb + 2SO_2$$

Whence the reducing power is found to be $\frac{1035}{120} = 8.6$

In the presence of an excess of sodium carbonate the sulphur is oxidized to trioxide as indicated by the following reaction:—

$$FeS_2 + 7PbO + 2Na_2CO_3 = FeO + 7Pb + 2Na_2SO_4 + 2CO_2$$

Which gives a reducing power of $\frac{1449}{120} = 12.07$

In order to get such a high reducing power as this it is necessary to have a very basic slag.

Any silica present combines with soda and litharge to form a silicate and if it is present in any considerable amount the litharge and soda are rendered unavailable for the higher oxidation of the sulphur.

The amount of lead reduces from any charge by any reducing agent is always a function of the temperature and the silicate degree. Other things being equal the more basic the charge the greater the amount of lead reduced by a unit quantity of the reducing agent. Thus, a certain sample of argols showed a reducing power of 11.04 when silica for a sub-silicate was added, 10.93 for a mono-silicate, 10.62 for a bi-silicate and only 9.26 for a tri-silicate.

The accompanying table gives the reducing power of some of the common sulphides. The theoretical figures are computed both for sulphur oxidized to SO_2 and SO_3. In the last columns are given the reducing power of the pure minerals using the following charge Na_2CO_3 5 gms., PbO 30 gms., SiO_2 2 gms., ore to yield an approximate 25 gram button.

TABLE XX. REDUCING POWER OF MINERALS.

Mineral	Formula	Computed		Actually Determined
		S to SO_2	S to SO_3	
Galena	PbS	2.6	3.46	3.41
Chalcocite	Cu_2S	3.9	5.2	
Arsenopyrite	$FeAsS$	5.7	6.96	8.18
Stibnite	Sb_2S_3	5.5	7.35	6.75
Chalcopyrite	$CuFeS_2$	6.2	8.44	7.85
Sphalerite	ZnS	6.37	8.5	7.87
Pyrrhotite	Fe_7S_8	7.35	9.9	10.00
Pyrite	FeS_2	8.6	12.07	11.05

Oxidizing Reactions. Certain metals notably iron, manganese, copper, cobalt, arsenic and antimony are capable of existing in two states of oxidation. When fused with a reducing agent the higher oxides of these metals are reduced to the lower state of oxidation at the expense of the reducing agent. Ores containing these higher oxides are said to have an oxidizing power on account of this property of using up reducing agent. For convenience this oxidizing power is measured in terms of lead although the bulk of the oxidizing reaction in any assay fusion is probably accomplished against the reducing agent of the charge.

For instance if in an assay fusion containing silica we have ferric oxide, sufficient for a bi-silicate, and carbon the following reaction takes place:—

$$2Fe_2O_3 + C + 4SiO_2 = 4FeSiO_3 + CO_2$$

From which we find that one gram of Fe_2O_3 requires 0.037 gram of carbon to reduce it to FeO. Expressed in terms of lead the relation would be as follows:—

$$Fe_2O_3 + Pb = 2FeO + PbO$$

That is to say the oxidizing power of Fe_2O_3 is $\frac{207}{160} = 1.3$

Similarly,

$$MnO_2 + Pb = MnO + PbO$$

The oxidizing power of MnO_2 is $\frac{207}{87} = 2.4$, which means that each gram of MnO_2 present in a fusion with litharge and a reducing agent will prevent the reduction of 2.4 grams of lead. It is easily seen therefore that this oxidizing power of ores must be taken account of in computing a furnace charge. The method of determining the oxidizing power of ores etc. will be discussed later.

In the crucible assay of high sulphide ores it is frequently necessary to add some oxidizing agent to the charge to prevent the reduction of an inconveniently large lead button. A lead button of 25 or 30 grams is usually sufficiently large to act as a collector of the precious metals and were a larger button obtained, it would entail an extra loss due to scorification or a prolonged cupellation as well as consuming extra time in this treatment. When therefore the ore charge would of itself reduce more than 25 or 30 grams of lead we ordinarily add potassium nitrate (niter) or some other oxidizing agent. Niter is almost exclusively used in this country for oxidizing. Its action with carbon is shown by the following equation:—

$$4KNO_3 + 5C = 2K_2O + 5CO_2 + 2N_2$$

From which the theoretical oxidizing power of niter expressed in terms of lead is found to be 5.17. The actual oxidizing effect of niter is always found to be lower than this due to the acidity of the charge and the probably escape of some oxygen.

In the soda-litharge-silica fusion such as commonly used in actual niter assays (sub-silicate), the reaction between niter and iron pyrite will be about as indicated by the following equation:—

$$10KNO_3 + 4FeS_2 + SiO_2 = Fe_4SiO_6 + 5K_2SO_4 + 3SO_2 + 5N_2$$

Assuming the reducing power of pyrite in this type of charge to be 10.0 the oxidizing power of niter is found to be 4.7.

A slight oxidizing effect may be obtained by using red lead (Pb_3O_4) in place of litharge and this is sometimes done especially in England and the English colonies. The oxidizing effect of red lead is shown by the following reaction:—

$$Pb_3O_4 + Pb = 4PbO$$

The oxidizing power in terms of lead is $\frac{207}{685} = 0.30$

Slags for Class 2 Ores. When an ore contains any considerable proportion of sulphide minerals and especially when they are present in such proportions that it is necessary to add niter to prevent the reduction of too much lead it will be found that the charges recommended for class 1 ores will not allow a satisfactory decomposition of the ore. Instead of obtaining two products, slag and lead, as the result of the fusion a third intermediate product (matte) is often obtained. This amounts to incomplete decomposition of the ore and is a sure indication of low results. The rate of melting down or the temperature of the furnace during the early part of the fusion seems to have a great deal to do with the formation of a matte. A rapid melting in a hot furnace seems to allow a more complete oxidation of the sulphur, possibly because the litharge is utilized for this purpose before it is locked up by the silica. At any event as rapid melting as may be without boiling over seems to give the most satisfactory results with class 2 ores.

A matte is much less likely to be formed, however, with a less acid charge and it has been found best therefore to make a slag approaching a sub-silicate for all heavy sulphide ores, as by this means more uniformly satisfactory results are obtained.

The Cover. In practically all crucible assay work it is customary to place on top of the mixed charge in the crucible a cover of some fusible substance. Different assayers advocate different materials as salt, borax, borax-glass, soda as well as different flux mixtures.

The idea of the cover is that melting early it makes a thick glaze on the sides of the crucible above the ore charge and tends to prevent sticking of particles of ore or lead globules which might be projected or left there by the boiling of the charge. As the fusion becomes quiet and the temperature rises, most of this glaze runs down to join the main charge and carries with it any small particles of ore or lead which may have stuck to it in the early part of the fusion.

The salt cover is thinly fluid when melted. It does not enter the slag but floats on top of it thus serving to keep out the air and to prevent loss by ebullition.

The borax cover fuses before the rest of the charge. It is thick and viscous when melted and serves to prevent loss of fine ore by "dusting", as well as to stop loss by ebullition. It finally enters the slag and so ceases to be a cover after the fusion is well under way.

Some assayers object to the use of salt on the ground that it is liable to cause losses of gold and silver by volatilization. It is a well known fact that gold chloride is volatile at a comparatively low temperature, commencing at 180° C. and that silver chloride is volatile in connection with the chlorides of arsenic, antimony, copper, iron, lead etc. When an ore contains substances such as manganese oxide, basic iron sulphate etc., capable of generating chlorine upon heating with salt it would seem wise to omit the use of salt. If it is not desired to use salt a good cover may be made from a mixture of borax-glass and sodium carbonate in the proportion of 10 parts of the former to 15 parts of the latter.

Testing Reagents. Each new lot of litharge and test lead should be assayed for silver and gold so that when any is found to be present a proper correction may be made. Different lots of argols, charcoal etc. are also found to vary in reducing power so that their reducing powers should also be determined.

The following procedure is designed, 1st, to allow the student to determine the reducing power of argols, charcoal or other reducing agents and at the same time to determine the silver correction for litharge, and, 2nd, to familiarize him with the principal operations connected with the crucible method of assay.

Procedure. Take two E or F pot furnace crucibles, or 12 or 15 gram muffle crucibles.

Weigh into them, in the order given the following:—

No. 1		No. 2.	
Sodium carbonate	5 grams	Sodium carbonate	5 grams
Silica	5 "	Silica	5 "
Litharge	60 "	Litharge	60 "
Argols	2½ "	Charcoal	1 "

Weigh the argols and charcoal on the pulp balance as exactly as possible, the others on the flux balance. Mix thoroughly with the spatula by turning the crucible slowly with one hand while using the spatula with the other. When finished tap the crucible several times with the handle of the spatula to settle the charge and to shake down any material which had lodged along the inside of the crucible above the charge. Finally put on a ½ inch cover of salt.

Pot Furnace Fusion. Have a good bright fire in the pot *furnace which should not however be filled with coke more than half way to the bottom of the flue.* Figure to so place the crucibles that their tops shall not be much above the bottom of the flue. Place a piece of cold coke directly under each crucible as it is put into the furnace. Cover the crucibles and pack coke around them being careful to prevent the introduction of any coke or dust. Close the top of the furnace, open the draft if necessary and urge the fire until the charges begin to fuse. Then close the draft and continue the melting slowly enough to prevent the charges from boiling over. When the charges have finished boiling, note the time and open the draft if necessary to get a yellow heat and continue heating for 10 or 15 minutes.

Pour the fusions into the crucible mold, which has been previously coated with ruddle, thoroughly dried and warmed. When cold, a matter of 5 or 10 minutes for a small fusion, break the cone of lead from the slag and hammer it into a cube to thoroughly remove the slag. Weigh the buttons on the pulp balance to the nearest tenth of a gram and record the weights and reducing powers in the note book.

Save the lead buttons and cupel them, using *selected* cupels. They should contain all of the gold and silver in the 60 grams of litharge used. Weigh the beads and part to see if gold is present. Record the weights of the beads and compute the correction for silver in 30 grams of litharge.

Muffle Fusion. If the fusions are to be made in the muffle have the muffle red and the fire under such control that the muffle can be brought to a full yellow in the course of a half hour. Melt at sufficiently low temperature to avoid violent boiling and then raise the temperature and pour as in the case of the pot furnace fusion.

Notes. 1. So-called silver free litharge can now be purchased but even this often carries traces of gold and silver.

2. In assaying samples of litharge low in silver 120 to 240 grams may be required to give a button of sufficient size to handle and weigh.

3. It is convenient to use litharge in multiplies of 30 grams and therefore the silver correction is based on 30 grams of litharge.

4. The temperature which the muffle should have before the crucibles are introduced depends upon the number of charges which are to be put in at one time. If only one or two the temperature should be low to avoid danger of boiling over. If, however the muffle is to be filled with crucibles the initial temperature may be higher as the crucibles can be depended upon to decidedly lower the temperature.

5. Pour the fusions carefully into the center of the molds and do not disturb until the lead has had time to solidify.

The following are the reducing powers of some of the common reducing agents.

Charcoal	23–30	Corn Starch	11.5–13
Argols	7–12.5	White Sugar	14.5
Flour	12–15	Cream of Tartar	4.5–6.5

Assay of Class 1 Ores. Gold or Silver.

This is the most common class of ores and as it is also the one which presents the fewest difficulties for the assayer, it is considered first. Actually, ores with no traces of sulphides are somewhat of a rarity but the methods given below may be adapted to ores containing moderate amounts of sulphides by simply decreasing the amount of reducing agent used.

Procedure. Carefully van some of the ore, estimate and record in the note-book the amount and character of each of the slag forming constituents and also of any sulphides present. If the ore is mainly siliceous weigh out one of each of the following charges:—

Charge (a).		Charge (b).	
Ore	0.5 A. T.	Ore	0.5 A. T.
Sodium carbonate	30 grams	Sodium carbonate	15 grams
Borax	3–5 "	Borax	3–5 "
Litharge	30 "	Litharge	50 "
Argols	*	Argols	*

* Argols enough combined with the reducing material of the ore to give a 25 gram button.

Weigh out the fluxes and place in the crucible in the order given and finally add the ore and argols last of all. Weigh the argols and ore on the pulp balance, the others on the flux balance. Mix thoroughly and place a $\frac{1}{2}$ inch cover of salt or soda-borax mixture on top.

Use F pot furnace crucibles, 15 or 20 gram muffle crucibles, if work is to be done in the muffle.

Fuse at a moderate red heat to avoid danger of the charge boiling over and when quiet raise the heat to a bright yellow. Allow 15 minutes of quiet fusion. Pour as usual, tapping the crucible gently against the mold if necessary to insure getting out the last globules of lead.

When cold, separate the lead buttons from the slag keeping them in order (a) (b). Record in the note-book the character and appearance of the slags, the ease or difficulty of the separation of each from the lead buttons, the appearance of the lead buttons and their greater or less malleability.

Weigh the lead buttons on the flux balance and cupel carefully to obtain feather litharge. Weigh the silver beads, correct for silver in the lithage used, part and weigh any gold found and finally report the value of the ore in oz. per ton.

Both of these charges should give good results on a siliceous ore. Charge (a) is a little less expensive, but charge (b) is more commonly used, as the slag contains two bases and the excess litharge will hold a moderate amount of impurities in solution. Charge (b) also gives a better separation of lead button and slag and has the further advantage that if the ore contains slightly more sulphides than was estimated the litharge will take care of them, giving a lead button free from matte. In charge (a), if we have more carbonaceous reducing agent plus sulphide mineral than the 30 grams of litharge can oxidize some of the sulphur will combine with various metals of the charge, principally lead, and form a matte which will appear immediately above the lead button.

Approximately 28 grams of litharge from each charge will be reduced to give the 25 gram lead button and is therefore not available to combine with the silica. The active[1] fluxes are then in charge (a), 30 grams of soda, 3–5 of borax, 2 grams of litharge and a little K_2O from the argols, totaling approximately $2\frac{1}{2}$ times the ore. In charge (b), the active fluxes are 15 grams of soda, 3–5 of borax, 22 grams of litharge and a small amount of K_2O, totaling approximately 3 times the ore. A very good rule to follow in making crucible charges is always to use at least $2\frac{1}{2}$ times as much active flux as ore.

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[1] By active fluxes is meant a flux which is to appear in the slag and therefore does not include the litharge which goes to form the lead button.

Borax in the charge should be increased as the bases increase. For an ore with 10 or 20 per cent of iron, manganese oxide or limestone add up to 10 or 15 grams of borax or 5 to 8 grams of borax-glass.

Notes. 1. Some assayers prefer to omit the borax from the charge and use a cover of crude borax or borax-glass in place of the salt. A borax cover may be used to advantage with ores which "dust" in the crucible, as the borax swells and melts early tending to catch and hold down the fine particles of ore which are projected upward from the charge.

2. The crucible should never be more than two-thirds full when the charge is all in.

3. If a silver assay alone is asked for it is customary to omit parting and report the combined precious metals as silver.

4. In assaying for gold alone if sufficient silver for parting is not known to be present, a piece of C. P. silver should always be added to the crucible or to the lead button before cupelling. If the approximate amount of gold is known allow about eight times its weight of silver.

5. The slag should be fluid on pouring and should be free from lead shot. If it strings out in long threads on pouring it is too acid. If it is pasty or lumpy, either the fusion has not been long enough to thoroughly decompose the ore, or the charge is too basic and more borax and silica should be added. The crucible should have a thin glaze of slag and should be but little corroded. It should show no particles of undecomposed ore or "shots" of lead. These latter can best be seen immediately after pouring and the student should make it a point to examine his crucible immediately after every pour. Neither the cover nor the outside of the crucible should show any glazing, as this indicates that the fusion has boiled over. The cold slag should be homogeneous, as otherwise it indicates incomplete decomposition of the ore. Glassy slags are usually preferred by assayers but are not essential to all ores.

6. If the button is hard or brittle or weighs more than 30 grams it should be scorified before cupelling. Hard buttons indicate the presence of copper, antimony, or nickel. Brittle buttons may be due to antimony, arsenic, zinc, sulphur, litharge or may be rich alloys of lead and the precious metals.

7. Examine carefully the line of separation of the slag and lead. The separation should be clean with no films of lead adhering to the slag. There should be no third substance between the slag and lead, nor should the surface of the lead show any disposition to crumble when hammered. Any lead gray, brittle substance between the lead and slag or attached to the lead button is probably matte. This indicates incomplete decomposition of the ore due to too short a time of fusion or to incorrect fluxing. If from the latter cause, decreasing the silica and increasing the soda and litharge will usually prevent its formation in a subsequent fusion.

8. For low grade gold ores or tailings a 1 A. T. charge is commonly used and for very low grade ores and tailings from 2 to 10 A. T. are run usually in the pot furnace. In using large charges of siliceous tailings the following charges more acid than the bi-silicate have been used with excellent results.

	Gold Ore	Low Grade	Tailings
Ore	1 A. T.	2 A. T.	5 A. T.
Sodium carbonate	30 grams	60 grams	150 grams
Borax	3–5 "	6–10 "	15–25 "
Litharge	60 "	90 "	180 "
Argols for a 25 or 30 gram button in each case.			
Crucible	G, 20 or 30 gm	H, 30 or 35 gm	K.

Assay of Class 2 Ores

Ores of this class containing only small amounts of sulphides are assayed exactly the same as class 1 ores using lesser amounts of argols. When however, sulphides are present in such amounts as to reduce a lead button too large to cupel (i.e. over 25 or 30 grams) a different method of procedure must be followed. The most important methods for the assay of these ores follow:—

1. **Scorification.** This method has already been considered. It is not well suited for gold ores and fails for many silver ores.

2. **Niter Method.** The reducing power of the ore is first determined by means of a preliminary assay. Using the figure thus obtained a certain amount of niter is added to the regular fusion to oxidize a part of the sulphur of the ore, thus preventing the reduction of too large a lead button. This is perhaps the most common method for the assay of sulphide ores. The sulphides are decomposed partly by litharge and partly by the niter.

3. **Iron Method.** The litharge added to the charge is kept low so that the lead from it plus that in the ore will yield a button of suitable size for cupelling. The sulphide minerals of the ore are decomposed by the means of the metallic iron. This is a very good method for many ores and is very commonly used.

4. **Roasting Method.** A carefully weighed portion of the ore is roasted to eliminate sulphur, arsenic, antimony etc. and the roasted ore is then assayed as a class 1 ore.

5. **Combination Wet and Fire Method.** The sulphides etc. of the ore are oxidized with nitric acid, the silver is precipitated as chloride and combined with the insoluble residue containing the gold, is assayed by either scorification or crucible.

Niter Assay. Preliminary Fusion. *Procedure:* Take from 2½ to 10 grams of ore depending on the amount of sulphide present, 2½ grams for pure pyrite, and correspondingly greater amounts for ores containing less sulphides. If the ore is mostly galena as much as 7 grams may be taken, the idea being always to get a button of 25 or 30 grams. (See reducing power of minerals.) Take the same amount of sodium carbonate as ore, 60 grams of litharge and up to 5 grams of silica. If the ore contains silica a proportionately less amount should be added. Use an E crucible for the pot furnace or a 12 or 15 gram crucible for the muffle. Weigh out the fluxes first, in the order given and place the ore on top mixing thoroughly with a spatula. Place a ½ inch cover of salt on top.

Fuse for 10 or 15 minutes finishing at a good yellow heat. Pour into crucible mold, allow to cool, separate the lead from the slag and weigh on the pulp balance to tenths of grams. Divide the weight of the lead by the weight of the ore taken to obtain the reducing power.

It should be noted that this reducing power is not an absolute thing but depends upon many factors such as the ratio of sodium carbonate to ore, the amount of borax, litharge and silica added as well as the temperature at which the fusions are conducted. The size of the lead button reduced in any fusion is decreased by any increase of the borax and silica and is increased by any increase of the litharge, soda or temperature.

The charge suggested for determining the reducing power of an ore gives as a rule slightly higher results than are obtained in the regular fusion, due to the large amount of litharge used in the preliminary fusion. This seems to be necessary however to insure the presence of a sufficient excess of litharge for all ores. The reducing power obtained in the regular assay is called the working reducing power, to distinguish it from that obtained in the preliminary fusion.

Estimating the Reducing Power of Ores. In many instances it is possible to estimate the reducing power of an ore within close limits. This requires a knowledge of the reducing powers of the common sulphide minerals (see Table XX), as well as the knack of vanning. The ore is vanned and the per cent of the various sulphides estimated, from which data the reducing power is found. For instance, if the ore is 50% pyrite and the rest gangue, the reducing power will be about 5.5 (50% of R. P. of pure pyrite). If it is 40% galena and 10% sphalerite, the reducing power will be 40% of 3.4 + 10% of 7.9 = 2.15 approximately. The reducing power of the ore being equal to the sum of the products of the reducing powers of the different constituents, multiplied by the percentage of each in the ore and the whole divided by 100.

In general if the amount of sulphides in the ore is comparatively small and especially if only 0.5 assay-ton of ore is used, it is a very simple matter to obtain a lead button of suitable size for cupelling by this means. If for example we have a mixture of galena and gangue mineral containing 50% of galena the reducing power of the ore will be $\frac{3.40}{2} = 1.70$ Using ½ assay ton of this ore we should obtain a lead button weighing 24.8 grams without either argols or niter. If we had estimated the galena at 40%, we would have added ½ gram of argols (R. P. 10) and would have obtained a 29.8 gram button which could still be cupelled. In a similar manner if we had estimated the galena at 60%, we would have added about 1 gram of niter and would obtain a button of about 20.8 grams, which is also all right for cupellation.

When we have practically pure sulphides, as in the case of pyrite or galena concentrates it is again easy to estimate the reducing power and properly control the size of the lead button.

Determining the Oxidizing Power of Niter. The oxidizing power of niter is found by fusing a weighed amount with an ore whose reducing power is known. To obtain comparative results the slags must be exactly like those used for the reducing power fusion and moreover to obtain the proper size of lead buttons in the final assay the slag that is made there must be similar as regards acidity, litharge excess etc. to that made in the preliminary fusion.

The following example illustrates the method of finding the oxidizing power of niter:—

Ore	5 grams	5 grams
Sodium carbonate	5 "	5 "
Litharge	60 "	60 "
Niter		4 "
Silica	5 "	5 "
Lead obtained	24.31 grams	6.61 grams

$$\text{Reducing power of ore } \frac{24.31}{5} = \overset{5.14}{4.86}$$

Lead oxidized by 4 grams of niter 24.31 − 6.61 = 17.70

$$\text{Oxidizing power of niter} = \frac{17.70}{4} = \underset{4.08}{4.42}$$

Niter Assay. Regular Fusion. Knowing the reducing power of the ore and the oxidizing power of niter we are ready to make up the charge for the regular assay. As in the case of class 1 ores it seems best always to use at least as much normal sodium carbonate as ore and we may start off on this basis. More litharge is used in this assay than in those previously discussed and assayers usually increase the litharge in proportion to the sulphur. The rule for the use of litharge proposed by Lodge is a good one and calls for 20 per cent in excess of the amount required to satisfy the reducing power of the ore. On account of the large amount of sulphur present a matte is often obtained if the acidity of the charge is not carefully controlled. It is therefore best in adding silica and borax to avoid using more than required for a sub-silicate.

The following examples may serve to show the method of computing charges. They are all based on 0.5 assay ton of ore as that is usually the maximum amount used for the niter assay. The litharge is computed according to Lodge's rule, then the silica required for the ore, soda, niter and active litharge is found and the rest of the computation is exactly like that discussed under class 1 basic ores.

	No. 1.	No. 2.	No. 3.
	90% Galena	50% FeAsS	90% FeS_2
	10% $CaCO_3$	50% SiO_2	10% SiO_2
	R. P. 3.15	R. P. 4.10	R. P. 9.50
Ore	0.5 A. T.	0.5 A. T.	0.5 A. T.
Sodium carbonate	15 grams	15 grams	15 grams
Borax-glass	5 “	5 “	10 “
Litharge	60 “	80 “	180 “
Niter (O. P. 4.2)	5 “	8 “	26.5 “
Silica	–	–	8.0 “

Procedure: Make up charges for your ores according to the rules outlined above. Conduct the fusions as for class 1 ores taking particular care when much niter is used until the boiling period is passed. As soon as all danger of boiling over has passed, heat rapidly to a full yellow and pour after 20 minutes of quiet fusion.

The following table of sub-silicate slag factors will aid in the determination of the quantity of acids to add.

TABLE XXI. SUB-SILICATE SLAG FACTORS.

Quantity of Bases	Quantity of Acids Required	
	Silica	Borax-glass
1 A. T. FeO	6.08 gms.	7.4 gms.
1 A. T. $CaCO_3$	4.40 “	5.37 “
1 A. T. $MgCO_3$	5.25 “	6.4 “
10 gms. PbO	0.67 “	0.82 “
30 “ Na_2CO_3	4.1 “	5.0 “
40 “ $NaHCO_3$	3.6 “	4.4 “
10 “ K_2CO_3	1.1 “	1.34 “

Notes. 1. It has been found possible to use somewhat less litharge than that necessary to satisfy the reducing power of the ore when a greater proportion of alkaline carbonate flux is used. This is probably due both to the oxidizing effect of CO_2 at a high temperature and to the solvent power of basic alkaline slags for matte.

2. As sulphide ores usually contain more or less copper, nickel, arsenic, antimony, zinc, tellurium and other so-called impurities, the large amount of litharge used serves the double purpose of helping to decompose the ore by oxidizing the sulphur and associated metals, and also tends to prevent these metal impurities from entering the lead button.

3. Aside from the inconvenience of the preliminary fusion the principal objection to the niter assay is due to the low results yielded. This is undoubtedly caused by the oxidation and slagging of the precious metals, particularly silver. To avoid this source of error only small amounts of niter should be used. When silver alone is being sought the niter may be entirely done away with by reducing the ore charge to a quantity sufficient to give a lead button weighing between 20 and 30 grams. In gold assays, however, a charge less than 0.5 assay ton is to be avoided as it fails to give a sufficiently close valuation of the ore.

4. Part of the oxidized precious metals may be recovered from the slag after the fusion is quiet by the addition of some reducing agent. For instance, if the fusion has been made in the muffle and without salt covers some crucibles of soft coal may be placed ni the mouth of the muffle after the fusions have become quiet. The smoke filling the muffle will enter the crucibles and reduce some lead from the slag which will in turn take with it part of the silver and gold.

The Iron Assay. The iron nail method of assaying sulphide ores is radically different from any of the other methods described. The principal difference being that metallic iron, usually in the form of nails, is used as the reducing and desulphurizing agent. As iron reduces lead from litharge this latter reagent is limited to 30 grams or less and to make up for this the quantity of alkali carbonate is increasing to two or three times that of the ore. Just before pouring the excess iron is removed.

The chemical reactions taking place in the crucible are entirely different from those of the other crucible methods. In the case of the argols, niter and roasting methods of assaying, the sulphides of the ore are oxidized by litharge, niter or the oxygen of the air and the sulphur either passes off as SO_2 and SO_3 or in the presence of sodium carbonate is converted into sodium sulphate which floats on top of the slag. In the iron assay, part of the sulphur is oxidized by the small amount of litharge used and the rest stays as sulphide, appearing either as an iron matte on top of the lead button or dissolved in the excess of basic slag.

The following reactions are illustrative of the chemical changes which take place. They are arranged in order of their occurrence.—

$$
\begin{aligned}
PbS + 2PbO &= 3Pb + SO_2 \\
Cu_2S + 2PbO &= 2CuPb + SO_2 \\
FeS_2 + 5PbO &= 5Pb + FeO + 2SO_2 \\
Fe + PbO &= Pb + FeO
\end{aligned}
$$

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99.1

when the litharge is all reduced the following occur

$$PbS + Fe = Pb + FeS \text{ (matte)}$$
$$FeS_2 + Fe = 2FeS \text{ (matte)}$$
$$Sb_2S_3 + 3Fe = 2Sb + 3FeS \text{ (matte)}$$
$$As_2S_3 + 13Fe = 2Fe_5As \text{ (speiss)} + 3FeS \text{ (matte)}$$
$$Cu_2S + Fe = Cu_2 + FeS \text{ (Partial)}$$

Finally, if there is a sufficient excess of alkali flux used, the iron matte is dissolved by this basic slag, probably as a double sulphide of iron and sodium or potassium.

From the equations it will be seen that copper, arsenic and antimony are reduced, at least in part, and go into the lead button, or in the case of arsenic form a speiss which ordinarily carries some of the precious metals. In general it may be said that the process is not suited for ores carrying much nickel, copper, cobalt, arsenic, antimony or tellurium. One or two per cent of copper in an ore does not interfere seriously with the assay, but when much more than this is present some other method should be chosen. Ores containing nickel are least of all suited to the process.

The slag made should not be more acid than a mono-silicate and probably a sub-silicate is better for most ores. Occasionally a matte is found on top of the lead button and this generally contains more or less gold and silver. It indicates a too acid slag, an insufficient amount of alkaline flux or too short a fusion. The slag although basic does not attack the crucible to any extent and crucibles may ordinarily be used a number of times.

The method is a most excellent one on suitable ores and the author's experience has been that in nine cases out of ten, students will obtain considerably higher results using this method than the niter method. It has the advantage that no preliminary fusion to determine the reducing power is necessary and that if the lead of the ore is allowed for, a button of the proper size for cupellation may always be obtained. As before mentioned the method is limited to pure ores and occasionally a hard button, or speiss may be obtained when no copper, antimony or arsenic was suspected in the ore. Occasionally also, but only when the slag is not properly constituted, or when the temperature of fusion is too high there may be difficulty in separating the lead from the slag and sometimes a thin film of lead may adhere to the slag when the two are broken apart. The only other objection is the difficulty of removing the nails free from shots of lead, but in general when the fusion has gone far enough this will not cause serious inconvenience.

Procedure: Pan the ore, estimate and record its mineral composition. Note especially the per cent of lead minerals. Use a G pot furnace or a 20 or 30 gram muffle crucible and weigh out one of the following charges.

	Pure Galena	½ Galena ½ Pyrite	Pyrite
Ore	0.5 A. T.	0.5 A. T.	0.5 A. T.
Sodium carbonate	30 grams	40 grams	50 grams
Borax	10 "	15 "	20–25 "
Litharge	20 "	27 "	35 "
Silica	2 "	2 "	2 "

Nails-from 3 to 5 (twenty-penny) cut nails or preferably one 3″ to 4″ track spike inserted point downward.

Cover Salt or borax-soda mixture.

Heat gradually to fusion, fuse from 40 to 60 minutes. Examine the nails occasionally and if badly eaten add several fresh ones, leaving the old ones in the crucible if they cannot be removed free from lead. Fuse until the nails may be freed from lead by tapping them gently and washing them around in the slag. Remove all nails and pour as usual. The slag will be black and should separate easily from the lead button.

Notes. 1. If the ore contains two or more grams of silica none need be added.

2. If bicarbonate of soda is substituted for the normal carbonate use a correspondingly greater weight.

3. This fusion requires a somewhat longer time than the niter fusion owing to the fact that time must be allowed for all of the charge to come in contact with the surface of the iron nails.

4. The lead may not start to drive in cupelling quite as rapidly as other buttons owing to a small amount of iron which is often present.

The Roasting Method. This method of assaying sulphide ores is rarely used, but might be used to advantage on very low grade pyritic ores, so will be briefly described.

Procedure: Take from 0.5 to 5.0 assay tons of ore and spread out in a well chalked roasting dish of sufficient size to allow of stirring without loss. Have the muffle at a dull red only and the fire so low that the temperature of the muffle may be held stationary or raised but slowly. Place the dish in the muffle and cover it if the ore contains minerals which decrepitate and keep it covered until danger from this source is passed. The ore should soon begin to roast. When fumes are noticed coming from the ore, check the fire and hold it at this temperature for some time stirring frequently. After all danger of fusing is over gradually raise the temperature stirring at intervals of 20 minutes or one-half hour. Finally heat to about 700° C. for one-half hour, when if the ore contains only sulphides of iron and copper, practically all of the sulphur will be removed. If there is any doubt about the roast being complete, remove from the muffle, add a small amount of charcoal and see if any odor of sulphur dioxide is noticed. If the ore contains zinc, a much higher temperature will be required to break up the zinc sulphate. It is not best, however, to carry the roasting temperature above 700° C.

If the ore is principally galena or stibnite, add an equal weight of fine sand or assay silica before commencing the roasting, which should be done at a very low temperature to prevent the fusion of the sulphides.

If the ore contains arsenic or antimony, the roasting operation is more difficult. The best conditions for the elimination of these elements are alternate oxidation and reduction at a low temperature. The presence of sulphur aids in the elimination of these elements due to the fact that their sulphides are volatile. To obtain the reducing action necessary for the elimination of arsenic and antimony take the partially roasted from the muffle, allow it to cool for a few moments, and then mix powdered charcoal or coal dust with it and roast at a dull-red heat until the coal is burned off. Then add more coal and re-roast. Repeat this until no more fumes of arsenic or antimony are noticed, then heat with frequent stirring to about 700° C.

After the ore is roasted, the dish is carefully cleaned out and the ore is charged into a crucible with fluxes and treated exactly as a class 1 ore. If the sulphide mineral was mostly iron, the ore will probably be found to have a slight oxidizing power due to the formation of Fe_2O_3 and Fe_3O_4 in the roasting.

The roasting method of assaying is slow and takes up much muffle space. It is open to the liability of serious mechanical and volatilization losses. Its most useful field would seem to be the assay of low-grade pyritic gold ores where a very accurate determination of gold is desired. The method usually gives low results in silver.

The combination wet and fire assay is used principally for the determination of gold and silver in copper and nickel matte, copper bullion, etc. A description of the method will be found in the chapter on bullion assay.

Assay of Class 3 Ores.

The principal ores belonging to this class are those containing some of the higher oxides of iron or manganese, i. e. Fe_2O_3, Fe_3O_4, MnO_2. These are reduced by carbon and tend to enter the slag as ferrous and manganous silicates respectively. If a charge was made up for these ores using only the ordinary amount of argols this might be all used up in reducing the oxides of the ore and no lead button would result. To remedy this the oxidizing power of the ore should be known before making up the charge.

To determine the oxidizing power of an ore, fuse a known weight of it, say 10 or 20 grams with a regular crucible charge for that amount of ore and a carefully weighed amount of argols of known reducing power sufficient to more than oxidize the ore. The weight of lead then, that the argols could reduce from an excess of litharge, minus the weight of lead obtained is evidently the amount oxidized by the ore. This weight divided by the weight of ore taken gives the oxidizing power.

Having determined the oxidizing power of the ore the assay is made in the same manner as for class 1 ores with the addition of the extra argols required.

The following table shows the proper size of crucibles for different charges.

TABLE XXII. SIZE OF CRUCIBLES FOR VARIOUS CHARGES.

Amount of Ore Taken	Character of Ore	Furnace	
		Pot	Muffle
½ A. T.	Siliceous	F	15 or 20 gms.
1 A. T.	“	G	20 or 30 “
2 A. T.	“	H	30 or 35 “
5 A. T.	“	K	
½ A. T.	Basic. Iron or Niter Fusions	G	20 or 30 “
1 A. T.	“ “ “ “ “	H	30 “

CHAPTER IX.

SPECIAL METHODS OF ASSAY.

The Assay of Telluride Ores. The determination of the precious metals in ores containing tellurium has always been considered more than ordinarily difficult. Results obtained by different assayers and even duplicate assays by the same man were often widely divergent. The literature of telluride ore assaying is extensive and none too satisfactory; however, it is safe to say that most of the reported differences between duplicates and different assayers have been due more to difficulties in sampling than to the chemical interference of the element tellurium. When it is considered that most of the telluride ores which are mined contain less than 0.1 per cent telluride mineral, it is apparent that more than ordinary care must be taken to insure obtaining a fair proportion of this in the final assay portion. The telluride mineral itself may contain 40 per cent of gold, so that one 100 mesh particle more or less in the assay portion may make a difference of several hundredths ounces of gold to the ton. To obviate as far as possible this lack of homogeneity, all telluride ores should be pulverized to at least 150 and preferably 200 mesh and then very thoroughly mixed before the assay portions are weighed out.

Effect of Tellurium. Tellurium is a close associate of both gold and silver and is difficult to separate from these metals either in the crucible, scorification or cupellation processes. It is not however often found in abundance, and even in high grade ores tellurium itself is found in comparatively small amounts. For instance, in two high grade ores used by Hillebrand and Allen in their experiments on the assay of telluride ores, containing respectively 15 and 19 oz. of gold per ton, there was tellurium amounting to 0.074 and 0.092 per cent respectively. It seems unreasonable to expect such small quantities of any element to influence seriously the results of a fire assay.

In order to study the effects of tellurium in the gold and silver assay it is necessary to experiment with ores or alloys containing much more tellurium than those above mentioned. The following facts regarding the behavior of tellurium in cupellation and fusion are mostly due to the work of Holloway,[1] Pease[1] and Smith,[2] whom we have to thank for co-ordinating and elucidating much information which was hitherto much scattered and of doubtful value.

Effect of Tellurium on Cupellation. The presence of tellurium in a lead button causes a weakening of the surface tension of the molten metal. The result is the metal tends to "wet" the surface of the cupel and this allows particles of alloy to pass into the cupel and others to be left behind to cupel by themselves on its surface forming minute beads. In the case of a button containing 10 or more per cent of tellurium with an equal weight of gold or silver, complete absorption may take place. As the proportion of lead in the alloy is increased, the amount of absorption becomes less, until when the lead amounts to 80 times the tellurium very little loss of precious metal occurs in a properly conducted cupellation. (Smith).

Tellurium is removed comparatively slowly during cupellation particularly in the early stages, as might be expected on comparing the heat of formation of its oxide with that of lead oxide. Rose[3] gives the following figures for the heat of combination of these metals with 16 grams of oxygen,—Pb to PbO 503 Cal., Te to TeO_2 386 Cal. To avoid danger of undue loss in cupellation of buttons from the assay of such ores, as much as possible of the tellurium should be removed prior to cupellation. It is also evident that large lead buttons (30 or more grams) should be allowed for in order that the ratio of lead to tellurium be high.

Silver in the alloy protects gold from losses due to the presence of tellurium. It appears to act as a dilutant for the gold and should always be added to every gold assay for this reason if no other.

In the case of imperfect cupellation, tellurium is retained by the bead and gives it a frosted appearance. In perfect cupellation the final condition of the tellurium is that of complete oxidation to TeO_2. Owing to its effect in reducing surface tension, resulting often in minute beads being left behind, it would be well to use a cupel having a finer surface when cupelling buttons containing tellurium. Smith states that the loss due to sub-division and absorption in this case is much less when a "patent" (magnesia) cupel is used. Losses of gold and silver by volatilization during properly conducted cupellation of lead buttons from ordinary telluride ores is extremely small.

Effect of Tellurium in Fusions. Tellurium was formerly thought to

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[1] The assay of Telluride Ores. G. T. Holloway and L. E. B. Pease, Trans. I. M. M., 17 p. 175.

[2] The Behavior of Tellurium in Assaying, Sydney W. Smith, Trans. I. M. M., 17 p. 463.

[3] Trans. Inst. Min. & Met. 14 p. 384.

be oxidized to the di-oxide during fusion and to go into the slag as a sodium or lead tellurate. Smith disagrees with this and argues that tellurates are decomposed at a red heat, and that lead tellurate is white, while he found the litharge slags obtained in the fusion of telluride compounds to be black. He believes that tellurium exists in the slag as the black monoxide (TeO).

The slag best suited to the oxidation and retention of tellurium in crucible assaying is a basic one containing a considerable excess of litharge. The temperature of fusion should be moderately low as a high temperature prevents the satisfactory oxidation and slagging of the tellurium, probably owing to the formation of lead silicates before the litharge has had time to oxidize the tellurium. Smith gives the following reaction for the oxidation of tellurium:—

$$2\ PbO + Te = Pb_2O + TeO$$

In support of this he claims to have found the black sub-oxide of lead in the slag.

Practically all authorities agree that the scorification process is not reliable for telluride ores. When a button from a crucible assay contains too much tellurium for direct cupellation Smith recommends fusing or "soaking" the button under an ample amount of litharge at a moderate temperature (700–900° C.).

Hillebrand and Allen used the following charges for ores containing from 15 to 19 oz. gold and 0.074 to 0.092 per cent tellurium.

Ore	1 A. T.	Litharge	180 grams
Sodium carbonate	30 grams	Reducing agent for 25 gram buttons	
Borax-glass	10 "	Silver	2½ to 3 times gold.

They find the slag losses no higher than with ordinary gold ores and no serious cupellation losses. With ores containing much more tellurium than the above, the quantity taken should be reduced and the rest of the charge maintained as before.

The Assay of Ores and Products High in Copper. Crucible methods for the assay of matte and ores high in copper have largely supplanted the older scorification method. This is due to the fact that a larger amount of pulp may be used for each individual assay, thus increasing the accuracy of the results. The copper is eliminated as it is in the scorification assay by the solution of its oxide in the basic lead oxide slag. The assay thus combines the advantages of the scorification with those of the crucible assay.

Perkins[1] has made a careful study of this process, and calls attention to the fact that the litharge used must be in proportion to the

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[1] The Litharge method of Assaying Copper Bearing Ores and Products, and the Method of Calculating Charges. W. G. Perkins, T. A. I. M. E., 31 p. 913.

amount of copper and other impurities in the ore. The amounts he uses are very large (from 137 to 300 parts PbO to 1 part Cu), and make the method an expensive one. Others have reduced this amount considerably, and still manage to get buttons which will cupel.

The Slag. The slag should be decidedly basic, for if we combine the litharge with large amounts of silica and borax, it will no longer retain its power of holding the copper in solution. A small amount of silica is necessary to prevent to some extent the action of the litharge upon the crucible. One part of silica to from 15 to 20 parts of litharge is generally allowed in the charge. *Borax* should be entirely omitted as it acts to decrease the copper holding capacity of the slag, and also causes boiling of the charge. Perkins states that the best results are obtained with a slag which exhibits when cooled and broken a somewhat glassy exterior gradually passing to litharge like crystals towards the center. The amount of crystallization which takes place is, of course, a function of the rate of cooling and will depend among other things upon the size of the charge, the temperature of the charge when poured, and of the mold, so that too much weight should not be given to the above. The slag should however be crystalline resembling litharge, and if dull or glassy throughout, indicates the presence of too much acid for a good elimination of copper.

Conduct of the Assay. On account of the very corrosive action of the litharge slag it is especially necessary that the fusion be made rapidly. The muffle should be hot to start (1000° to 1100° C.), the hotter the better, and the fusion should be finished in from 20 to 30 minutes. This not only preserves the crucibles, but also as a necessary sequel prevents the slag from becoming charged with silica and thus forcing the copper into the button. The slag melts at a low temperature and a very high finishing temperature is not necessary. With a quick fusion there is less chance for oxidation of lead with the consequent reduction of too small a lead button.

For the best work the hole in the back of the muffle should be stopped up, and a reducing atmosphere maintained in the muffle. This may be accomplished by filling the mouth of the muffle with charcoal or coke, or by distributing a few crucibles part full of soft coal throughout the charge and using a tight-fitting door. If this precaution is not observed part of the silver will be oxidized and lost in the slag.

The following charges kindly furnished by the Boston and Montana Reduction Department of the Anaconda Copper Mining Company, Great Falls, Montana are recommended for these ores.

TABLE XXIII. CHARGES FOR COPPER BEARING MATERIAL.

Material	Approximate Analysis		Charge for Silver (In 20 gram crucible)		Charge for Gold (In 30 gram crucible)	
Concts.	Cu	9%–15%	Sample	$\frac{1}{2}$ A. T.	Sample	1 A. T.
	SiO	15%–23%	Soda	20 grams	Soda	30 grams
	FeO	33%–40%	Litharge	100 "	Litharge	150 "
	S	33%–40%	Silica	5 "	Silica	8 "
	Ag	3 oz.–5 oz.	Niter	15.25 "	Niter	40–60 "
	Au	0.015oz.–0.025oz.	Cover mixture		Cover mixture	
Matte	Cu	30%–45%	Sample	$\frac{1}{4}$ A. T.	Sample	$\frac{1}{2}$ A. T.
	Fe	40%–30%	Soda	18 grams	Soda	25 grams
	S	30%–27%	Litharge	100 "	Litharge	200 "
	Ag	10 oz.–18 oz.	Silica	7 "	Silica	12 "
	Au	0.07 oz.–0.11 oz.	Niter	6 "	Niter	18 "
			Cover mixture		Cover mixture	
Matte	Cu	45%–60%	Sample	$\frac{1}{4}$ A. T.	Sample	$\frac{1}{2}$ A. T.
	Fe	30%–15%	Soda	18 grams	Soda	25 grams
	S	27%–24%	Litharge	125 "	Litharge	240 "
	Ag	15 oz.–25 oz.	Silica	7 "	Silica	12 "
	Au	0.10 oz.–0.14 oz.	Niter	4 "	Niter	14 "
			Cover mixture		Cover mixture	

Assay of Antimonial Gold Ores. The niter method is universally recognized as being the best method for the sulphide ores of antimony. Considerable litharge is necessary to keep the antimony out of the lead button. The following charge is recommended by two English authorities:[1]—

Ore	$\frac{1}{2}$ A. T.	Litharge	100–120 grams
Na_2CO_3	10–20 grams	Niter	19 "
Borax-glass	5–10 "	Silica	10 "

A preliminary assay to determine the reducing power is of course necessary. The above charge will be found to correspond almost exactly with our standard for sulphide ores, with litharge according to Lodge's rule.

George T. Holloway in discussing this method recommended using a much larger proportion of soda in the charge, i.e., three times as much as stibnite, in order to aid in the retention of the antimony in the slag as a sodium antimoniate.

Assay of Auriferous Tinstone. C. O. Bannister[2] finds a crucible assay with the following charge to be the most satisfactory method:—

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[1] William Kitto, Tr. Inst. of Min. & Met., 16 p. 89.

[1] William Smith, Tr. Inst. of Min. & Met., 9 p. 332.

[2] Trans. Inst. of Min. and Met. (London) 15 p. 513.

Ore	25	grams
Sodium carbonate	40	“
Borax	10	“
Red lead	60	“
Charcoal	1.5	“

In this method the tin is converted into a fusible sodium stannate. The author found no tin reduced during the fusion as shown by the button cupelling without difficulty. In all ores carrying over 1 oz. of gold per ton, the slags were cleaned by a second fusion with 10 grams of soda, 30 grams of red lead and 1.5 grams of charcoal.

Various other methods of assay were tested but none were as satisfactory as this.

Corrected Assays. In the assay of high-grade ores and bullion it is often desirable to make a correction for the inevitable slag and cupel losses. This is done in one of two ways: either *by the use of a "check" or synthetic assay or by assaying the slags and cupels* resulting from the original or commercial assays.

In correcting by a "*check*" assay a preliminary assay is first made and then an amount of proof silver or gold, or both, approximately equivalent to the amount present in the sample, is weighed out and made up to approximately the composition of the sample by the addition of base metal, etc. The check thus made is assayed in the same furnace parallel with the real assay. Whatever loss the known amounts of precious metal in the check sustain is added to the weight of metal obtained from the sample as a correction, the sum being supposed to represent the actual metal present in the sample. This method of correction is always used in the assay of gold and other precious metal bullions, and is sometimes used in the assay of high-grade ores. A more detailed description of the method will be found in the chapter on the assay of bullion. This method when properly applied is the better and gives a very close approximation to the actual precious metal contents of a sample.

In the case of rich ores and furnace products other than bullion, a correction is usually made by assaying the slags and cupels resulting from the original assay. The metals thus recovered are added as a correction to the weight first obtained. This method, while approximating the actual contents of an ore, may occasionally give results a little too high, for although gold and silver lost by volatilization is not recovered and the corrections themselves must invariably suffer a second slag and cupel loss, yet on the other hand, the cupelled metal from both the first and second operations is not pure and may retain enough lead and occasionally other impurities from the ore to more than offset the above small losses. The results of assays corrected by this method are evidently somewhat uncertain, but are nevertheless much nearer to the real silver content than are the results of the uncorrected or ordinary commercial assay.

Smelter contracts are almost invariably still written on the basis of the ordinary or uncorrected assay and when the corrected assay is made the basis of settlement, a deduction is made amounting to the average correction. This amounted to 1.1 per cent in the case of certain Cobalt ores.

When a corrected assay is to be made it is well to use a Portland cement or magnesia cupel for the first cupellation as these materials are easier to flux than bone-ash.

To assay a Portland cement cupel the following charge, a sesqui-silicate, is found to give satisfactory results:—

Cupel (45 grams of cement).
Na_2CO_3—45 grams.
Borax-glass—21 grams.
Litharge—Dependent on size of original button, to make a total of 75 grams.
Argols (R. P. 10) 3.2 grams.
Silica—32 grams.

To assay a magnesia cupel, good results are obtained by adding soda equal to the original weight of the cupel and litharge to make a total of 30 grams more than the original weight of the cupel (allowing for litharge in the cupel). Compute the silica necessary to make a sesqui-silicate with magnesia, soda and active litharge, and add two-thirds of this weight of silica and substitute for the other third twice its weight of borax-glass.

To assay a bone-ash cupel, first remove and reject the unsaturated part of the cupel in order to have as little of this refractory material as possible to deal with. The saturated part will be about 50 per cent bone-ash and 50 per cent litharge. Grind to 80 mesh and clean the bucking board or machine by grinding 10 or 15 grams of 10 mesh silica. This should be reserved and added to the charge. To assay, add a weight of soda equal to the weight of saturated cupel material, two-thirds as much borax-glass, 25 grams of litharge plus enough more to make a total equal to the weight of saturated cupel material, silica one-third as much cupel material, reducing agent for a 22 gram lead button. For example:—

Cupel material	45 grams	Litharge	47½ grams
Na_2CO_3	45 “	Argols (R. P. 10)	2.2 “
Borax-glass	30 “	Silica (from cleaning board)	15 “

CHAPTER X.

THE ASSAY OF BULLION.

Bullion from an assayer's point of view is an alloy containing enough of the precious metals to pay for parting.

The different bullions are usually named to correspond with their major components, for instance, copper bullion an alloy of copper with small amounts of other impurities, as well as some gold and silver. In the same way we have lead, silver and gold bullions. Doré bullion is silver bullion containing gold. The term base bullion is used in two different senses. According to the lead smelters definition base bullion is argentiferous lead, usually the product of the lead blast furnace; according to the mints and refiners definition it is bullion containing from 10 to 60 per cent of silver, usually some gold, and a large percentage of base metals particularly copper, lead, zinc and antimony. Fine gold bars are those which are free from silver and sufficiently free from other impurities to make them fit for coinage and use in the arts usually 990 to 999 fine.

The results of lead and copper bullion assays are reported in ounces per ton as in the case of ore assays, but in the assay of silver, gold and doré bullions the results are reported in "fineness," i.e., so many parts of silver or gold in one thousand parts of bullion. Thus sterling silver is 925 parts fine, that is to say, it is 92.5 per cent silver.

Weights. In assaying gold, silver and doré bullion, a special set of weights called gold assay weights are used. This is termed the "millime" system, and the unit one millime weighs 0.5 milligram, and therefore the 1000 millime weight equals 0.5 grams. Ordinary weights in the gram system may be used but as 0.5 gram is the quantity of bullion commonly taken for assay the use of the millime system saves computation in obtaining the fineness.

Sampling Bullion.

Bullion may be sampled either in the molten or in the solid condition. When it may be melted and kept free from dross the dip or ladle sample is usually the more accurate method. As the weight, as well as the assay of the bullion must be known in order to value it, the sampling of large lots of bullion by the dip sample method often presents difficulties owing to changes in weight or purity in the considerable length of time necessary for pouring. Again it is not always convenient to melt a lot of bullion to obtain a sample, and other means must be found. Sampling solid bullion by punching, boring, sawing or chipping, under certain conditions, may be made to yield good results. Lead bullion is usually sampled by punching one or more holes in each bar, and combining and melting the punchings. Copper bullion is now generally cast in the form of slabs or anodes, and these are drilled.

Sampling Molten Bullion. The most satisfactory method of sampling bullion is to melt the whole in a suitable vessel, stir thoroughly with a graphite rod or iron bar to mix and then immediately before pouring, ladle out a small amount and granulate it by pouring into a pail of water. If these operations are correctly performed there is no chance for segregation, and each particle of the granulated metal should be a true representative of the whole. If a granulated sample is not desired, a ladleful of the mixed molten metal may be poured into a thick-walled flat mold so that it chills almost instantly, and a drill or saw sample may be taken from this. When a ladle sample is taken, the ladle must be so hot as not to allow the forming of any solidified metal or "sculls" as this would interfere with the homogeneity of the sample. This method of sampling is most satisfactory on bullions which do not oxidize or form dross on melting, as this of course, adds a complication hard to allow for.

Sampling Solid Bullion. The principal difficulty in the sampling of bullion in the form of bars or ingots is caused by the segregation of the various metals in cooling. If it were possible to cool a bar instantly, segregation would be prevented, and a chip or boring taken from any part would be representative. As instant cooling is impossible, the sampling of bars of the ordinary dimensions becomes a difficult problem. As the result of a careful study of this problem Keller[1] has concluded that it is almost impossible to obtain samples of satisfactory accuracy from bars or pigs of the usual dimensions. To eliminate the difficulties of sampling from a bar he recommends casting the metal in the form of a thin plate. Of course some concentration would take place here also, but as the plate would solidify so much faster than the same metal cast in a bar or ingot this factor would have less weight. Owing to the fact that concentration takes place from or toward every surface, we will have all around the plate a zone not wider than the thickness of the plate where concentration has taken place both horizontally and vertically, but which should

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[1] T. A. I. M. E., 27, p. 106.

of itself be a sample of the whole. In the part of the plate enclosed by this zone we have concentration in the vertical direction only. If we drill or punch through this part of the plate we should obtain a correct sample of the whole. Keller cites experiments to prove the above theory.

Some typical methods of sampling lead and copper bullion follow.

Sampling Lead Bullion. Lead bullion is sampled both in the liquid and in the solid state. In either case it is now customary to transfer the lead from the blast furnace either into a reverberatory furnace or into large kettles holding 20 to 30 tons. Here it is purified either by liquation, or by cooling to a little above the melting point of pure lead. By doing this, a large part of the impurities which are held in solution by the superheated lead are separated out as a dross which is carefully removed by skimming. The remaining lead, which is now in a better condition to sample, is drawn off by means of a syphon and cast into bars of about 100 pounds.

In taking a *dip sample* a small ladleful is taken at regular intervals from the stream coming from the syphon. These individual samples are carefully remelted at a dark red heat in a graphite crucible, the melt is well stirred and cast in a heavy-walled shallow mold, making a cake about 10″ long, 5″ wide and ½″ thick. This cools so quickly that there is little or no chance for segregation. The final assay samples are taken from this cake either by sawing and taking the sawdust, or by boring entirely through the slab in a number of places, and taking the borings, or by cutting out four or more ½ A. T. pieces from different parts of the bar and using these directly.

In *sampling solid lead bullion* the bars are sampled by means of a heavy punch which takes a cylindrical sample about 2″ long and 1/8″ in diameter. There are naturally a number of different systems but the most common method is to place five bars side by side and face up, and punch a hole in each extending half-way through. Each bar is punched in a different place and in such a way that the holes make a diagonal across the five bars. The bars are then turned over and another sample is taken from each along the opposite diagonal. Usually one carload of about 20 or 30 tons is sampled as one lot. The punchings from such a lot, weighing from 8 to 15 pounds are melted in a graphite crucible and cast into a flat bar, from which the final assay samples are taken by sawing, drilling or cutting.

Sampling Copper Bullion. The sampling of copper bullion may be classified into smelter methods, and refinery methods. The bullion is quite universally cast in the form of anodes at the smelter, and shipped to the refinery in this form. This renders remelting at the refinery unnecessary, and the result is that the refiners sample the solid bullion by drilling. The smelters, having the bullion in the molten condition, generally sample it in this condition on account of the greater ease and less expense.

Probably the most satisfactory smelter method of sampling is the "splash shot method", which consists in shotting into water a small portion of the molten stream of copper as it flows from the refining furnace by "batting" the stream with a wet stick. This operation is repeated at uniform intervals during the pouring, the amount taken each time being kept about the same. The samples are dried and dirt and pieces of burned wood are removed. All material over four mesh and under 10 mesh is rejected, and the remainder taken as the sample. This method when properly carried out gives results which check within practical limits with the drill sample of the anodes taken at the refinery.

Another method which is used to some extent for sampling molten copper bullion is known as the "ladle-shot method." This consists in taking a ladleful from the furnace or from the stream of the casting machine and shotting it by pouring over a wooden paddle into water. In this method at least three ladlefuls are taken, one near the beginning, one at the middle, and one near the end of the pour. The shots are treated in the same manner as before. This method is not thought so well of as the previous one on account of segregation toward or from the " sculls " which are left in the ladles.

Instead of shotting and taking the shot for the final sample, W. H. Howard of Garfield, Utah, recommends ladling into a flat disc. This "pie sample" is sawed radially a number of times, and the sawdust used for the final sample.

The following description of the method of sampling anodes at Perth Amboy, N.J. is typical of refinery methods of sampling and is the method developed by Dr. Edward Keller. The copper is received in the form of anodes 36″ long, 28″ wide and 2″ thick. These are carefully swept to remove foreign matter, and then drilled with a 0.5″ drill completely through the anode, all of the drillings being carefully saved. A 99-hole template is used to locate the holes which are spaced 3 1/16″ center to center, and the outside row is approximately $2\frac{1}{2}$″ from the edge of the anode. The holes of the template are used in continuous order, one hole to the anode.

For very rich anodes some refiners use a template having as many as 240 holes, but it seems doubtful if this arrangement of spacing a single hole in each anode will yield any better sample.

With low-grade, uniform bullion every fourth anode only is drilled. A 30 ton lot of anodes in which each one is drilled will yield 6 or 8 pounds of drillings, which are ground in a drug-mill fitted with manganese steel plates and reduced by quartering to about 2 pounds. This sample is reground until it will all pass a 16-mesh screen and is then divided into the sample packages.

The Assay of Lead Bullion.

A description of the cupellation assay of lead bullion has already been given in the chapter on cupellation. In smelter control work the assay is usually made in quadruplicate. If the bullion contains sufficient copper, arsenic, antimony, tin or other base metals to influence the results of the cupellation assay, three or four portions of 0.5 or 1.0 A. T. are scorified with the addition of lead until the impurities are eliminated, when the resultant buttons are cupelled.

Correction for Cupel Loss. In some instances the slags and cupels are re-assayed and the weight of the gold and silver found is added to that obtained from the first cupellation. There is no fixed custom as yet regarding the use of corrected assays. In most of the custom smelters, the uncorrected assay is used as the basic of settlement; but some of the large concerns who have their own refineries are using the corrected assay in their inter-plant business.

The Assay of Copper Bullion.

Copper bullion may be assayed by the scorification, crucible or by a combination of wet and fire methods. In the combination method the bullion is treated with sulphuric or nitric acid which dissolved the copper and the silver and leaves the gold. The silver is precipitated by suitable reagents and filtered off together with the gold. The filter paper and contents are put into a scorifier or crucible with reagents and the assay finished by fire methods.

The scorification method is generally accepted as standard for gold, and many smelter contracts state that "gold shall be determined by the all fire method or its equivalent." The mercury-sulphuric acid combination method on many bullions gives gold results equal to the scorification. The silver results obtained by the scorification method are open to suspicion owing to the considerable slag and cupellation losses, and the doubt concerning the purity of the buttons, which often contain noticeable amounts of lead and copper.

The crucible method has not as yet come into common use for the determination of gold and silver in copper bullion, but according to

Perkins[1] it gives gold results equal to the "all-scorification" method.

In smelter practice, silver in copper bullion is determined usually by the nitric acid combination method, sometimes by the mercury-sulphuric acid combination method. This later method tends to give high silver results, owing to the incomplete solution of the copper in the acid, and the possibility of some copper being retained in the silver bead.

The nitric acid combination method is recognized as giving low results in gold. Van Liew[2] attributes this to the solution of the gold in the mixture of nitrous and nitric acids present. He found a decided loss (33.7%) of gold on treating gold leaf with a mixture of nitrous and nitric acids for two and a half hours. He gives a method of slow solution in cold dilute acid which reduces this loss to a minimum.

The Scorification Method. The following method commonly referred to as the "all fire" method is a modification kindly supplied by Mr. H. D. Greenwood, Chief Chemist for the United States Metals Refining Co., Chrome, N. J.

Sample down the finely ground bullion on a split sampler in such a way as to obtain a sample of about 1 A. T., which will include the proper proportion of finer and coarser parts of the borings. This sampling must be conducted carefully, as the precious metal contents of the finer parts differs somewhat from that of the coarser portion of the sample. Portions "dipped" from the sample bottle or from the sample spread out on paper are likely to contain undue amounts of coarse or fine.

Weigh out 4 portions of copper borings of $\frac{1}{4}$ assay ton each, mix with 50 grams test lead, put in 3-inch Bartlett scorifiers, cover with 40 grams test lead and add about 1 gram SiO_2. Scorify hot, heating at finish so as to pour properly. Add test lead to make weight of button plus test lead equal to 70 grams, add 1 gram SiO_2 and scorify rather cool. Pour, make up to 60 grams with test lead, adding 1 gram SiO_2 and scorify.

Combine the buttons two and two, and make up each lot to 85 grams with test lead, adding 1 gram SiO_2 and scorify very cool. Make up button to 70 grams by adding test lead, add 1 gram SiO_2 and scorify for the fifth time. The buttons should be free from slag and weigh 14 grams.

Cupel at a temperature to feather nicely, and raise heat at finish. Cupels to be made of 60 mesh bone-ash, and to be of medium hardness.

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[1] T. A. I. M. E., 33 pp. 671.

[2] E. & M. J. 69, pp. 496, et seq.

Weigh the bead and part as usual. Dry, anneal and weigh. The two results should check within .02 oz. per ton, and the average figure is to be reported. If the silver contents of the bullion is low, add enough fine silver to the copper borings before the first scorification to make the total silver in the mixture equal to about 8 times the amount of gold.

The Crucible Method. The crucible method for gold and silver in copper bullion was first described by Perkins[1] and as described by him showed no great advantage over the scorification method as to saving in time or cost of materials, or increased furnace capacity. The following modified procedure requires about one-third of the materials, time and furnace capacity as that described by Perkins, and yet gives buttons sufficiently free from copper so that they may be cupelled direct.

Sample down the finely ground bullion to about ¼ A. T. and adjust the weight of the sampled portion to exactly ¼ A. T. Place in a 20 gram crucible and mix with it 1.2 grams of powdered sulphur. Cover this with a mixture of 15 grams of sodium carbonate, 240 grams of litharge, and 8 grams of silica; but do not mix with the sulphur and copper which should be allowed to remain in the bottom of the crucible. Cover with salt or flux mixture and place in a hot muffle so that the charge will begin to melt in 6 or 8 minutes. The fusions should be quiet and ready to pour in 25 or 30 minutes.

If a salt cover is used the lead buttons should weigh about 32 grams, if a flux cover is used they may be somewhat smaller. With a properly conducted assay the buttons are soft enough for direct cupellation; but the cupels are quite green. If the assayer prefers, the buttons may be made up to 50 or 60 grams with test lead and scorified in a 3 inch scorifier to further eliminate the copper. After cupellation the buttons are weighed and parted as usual. It is well to do four fusions, and to combine the buttons two and two for parting.

Remarks. As soon as the sulphur melts (115° C.) it combines with the copper to form a matte which is decomposed and most of its copper oxidized and slagged by the litharge of the charge. The fusions melt down very quietly almost without boiling, and with a short period of fusion the crucibles are not badly attacked. The final temperature need not be higher than a good bright red or full yellow. The slag is heavy but very fluid and should not contain any lead shots.

The method gives results in gold equal to the scorification method;

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[1] An "All-Fire" Method for the Assay of Gold and Silver in Blister Copper. W. G. Perkins, T. A. I. M. E., 33 pp. 670.

but like any method using high litharge, the silver is apt to be somewhat low.

Mercury—Sulphuric Acid Method. Sample down the finely ground bullion on a split sampler in such a way as to obtain a sample of about 1 A. T., which will include a proper proportion of the finer and coarser parts of the borings. This sampling must be conducted carefully as the precious metal contents of the finer parts differs somewhat from that of the coarser portion of the sample. Portions "dipped" from the sample bottle or from the sample spread out on paper are likely to contain undue amounts of the coarse or fine.

Adjust the weight of the sampled portion to exactly 1 A. T. and transfer it to a No. 5 beaker (capacity about 750 c.c.). The beaker should have a watch glass cover.

Treat the sample with 10 c.c. of mercury solution and shake the beaker until the copper is thoroughly amalgamated; then add 80 c.c. of strong sulphuric acid, place the beaker on a hot plate and boil until the copper is dissolved. This requires about twenty minutes.

Remove the beaker and allow it to cool. The contents will be a semi-liquid sludge. When cool, add about 100 c.c. of cold water and mix; then add about 450 c.c. of boiling water and stir until the copper sulphate dissolves.

Bring to boiling and add 4 to 6 c.c. of salt solution, 1 c.c. equivalent to 50 mg. Ag. Remove from the hot plate and add 10 c.c. of a 10 per cent solution of lead acetate. Stir well, allow to settle and filter at once through double filter papers (12½ or 15 c.m.) washing the beaker with hot water. Finally wipe the inside with filter paper and add it to the filter. Thorough washing of the filter is not necessary.

Transfer the wet filter and its contents to a 2½″ scorifier which has been glazed on the inside by melting litharge in it and pouring away the excess.

Burn off the filter paper at a low temperature—best in a closed oven which may be heated to, say 175° C. This chars the paper slowly without danger of loss of silver.

When the paper is consumed, add 30 grams of test lead and scorify; pour so as to obtain a 12 gram button, cupel as usual to produce feather litharge, weigh the gold and silver bead and part with dilute nitric acid.

The mercury solution mentioned above is made by dissolving 100 grams of pure mercury in nitric acid, and diluting to 500 c.c. From this stock solution take 50 c.c. and dilute it to 1 liter, for the working solution—10 c.c. of the latter will serve for each assay-ton of copper bullion.

The object of adding mercury is to secure an easy solution of the copper in sulphuric acid. If the copper is treated directly without previous amalgamation, it is very difficult to dissolve it in sulphuric acid. In fact a considerable portion of it will remain insoluble, partly in the form of sulphide of copper. If the copper be amalgamated on the other hand, solution proceeds smoothly until practically all of the copper is dissolved. When the bullion is low in precious metals, say less than 50 ounces per ton, no silver dissolves in the sulphuric acid. No gold dissolves whatever the grade. If the bullion is very rich in silver a little of it may dissolve in the acid.

The assays should be made in duplicate or triplicate, and the average results reported. Differences on silver seldom exceed 0.2 ozs.; on gold the results are usually exactly the same. The sulphuric acid used should be chemically pure and full strength (1.84 sp. gr.).

Nitric Acid Combination Method.[1] Sample down the finely ground bullion on a split sampler in such a way as to obtain a sample about 1 A. T., which will include the proper proportion of the finer and coarser parts of the borings. This sampling must be conducted carefully as the precious metal contents of the finer parts differ somewhat from that of the coarser portion of the sample. Portions "dipped" from the sample bottle or from the sample spread out on paper are likely to contain undue amounts of coarse or fine.

Weigh out two portions of copper borings of 1 A. T. each, and carry the assay through on each portion as follows:—

Place in a No. 5 beaker, add 100 c.c. of distilled water and 90 c.c. HNO_3, sp. gr. 1.42, the latter being added in portions of 30 c.c. each at intervals of about 1 hour. When all is in solution precipitate a small amount of silver chloride with salt solution in order to collect the gold, filter through double filter papers and wash the filter papers free from copper. To the filtrate add the calculated amount of salt solution to precipitate all the silver and a slight excess, measuring the solution with a burette and varying the amount added with the richness of the bullion. Allow to stand over night after stirring well. Filter the silver chloride through double papers, wash papers free from copper, then sprinkle 5 grams of test lead in the filter paper and fold into a $2\frac{1}{2}$ inch Bartlett shape scorifier, the bottom of which is lined with sheet lead. To this add also the filter papers containing

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[1] Procedure kindly supplied by Mr. D. H. Greenwood, Chief Chemist, for the United States Metals Refining Company, Chrome, N. J.

the gold. Dry and ignite the filter papers carefully, cover with 35 grams of test lead, a little borax-glass, and scorify at a low heat so that the resultant button will weigh about 12 grams. Cupels should be feathered nicely. Cupel to be made of 60 mesh bone-ash and to be of medium hardness. Weigh the bead and part. Anneal and weigh the gold. The two results on gold should check within 0.02 oz. per ton, and the silver within 1 per cent.

The Assay of Doré Bullion.

This method is the one generally adopted by assayers in this country, and may also be used for the assay of silver bullion. A better method for the accurate determination of silver in doré or silver bullion is probably the Gay-Lussac or salt titration, also known as the mint method. This later method requires considerable equipment and preparation and for this reason the occasional assay is more easily done by fire methods.

The Check. In order to correct for the inevitable losses in cupelling as well as for any other errors in the assay, silver, doré, and gold bullions are always run with a check. This check or "proof center" is a synthetic sample made up of known weights of pure silver, gold and copper to approximate as closely as possible the composition of the bullión to be assayed. It is cupelled at the same time and under the same conditions as the regular assays, and whatever gain or loss it suffers is added as a correction to the regular assay. To obtain data to make up the check a preliminary assay is made to determine the approximate composition of the bullion.

Preliminary Assay. A sample of 500 mgs. of bullion or as near this amount as possible is weighed out on the assay balance, and the exact weight recorded. This is compactly wrapped in 6 or 8 grams of lead foil and cupelled in a small cupel with feather crystals of litharge. The cupel should be pushed back in the muffle for the last two or three minutes to insure the removal of the last of the lead. After the play of colors has ceased it should be drawn toward the front of the muffle and then covered with a very hot cupel to prevent sprouting. It is then removed gradually from the muffle and when cool is cleaned, weighed and parted in the ordinary manner. The gold will require more than the ordinary amount of washing on account of the large quantity of silver present.

If the cupelling has been properly conducted it will be fair to assume a loss of one per cent of silver in determining the approximate silver. The weight of gold may be taken as approximately correct. The sum of the weights of approximate gold and silver is subtracted from the weight of bullion taken to obtain the amount of base metal. This will usually be copper, but whatever it is the assayer should be able to determine by the appearance of the bullion and the cupel.

Final Assay. Two portions of approximately 500 mgs. are weighed accurately and wrapped in the proper amount of lead foil as shown by the following table which assumes the impurity to be copper.

TABLE XXIV. LEAD RATIO IN CUPELLATION.

Fineness of Au. + Ag.	Wt. of Lead	Fineness Au. + Ag.	Wt. of Lead
950	5 gms.	750	11gms.
900	7 "	700	12 "
850	8	650	13 "
800	10 "	600	15 "

A check is made up with C. P. silver and proof gold equal to the approximate silver and gold found by the preliminary assay and the necessary amount of copper or other base metal. These are wrapped up in the same amount of sheet lead as was used for the bullion. The lead for these assays is best cut into equal sized rectangles with proportions approximately $1\frac{1}{2}'' \times 2\frac{1}{2}''$, and twisted into the shape of little cornucopias with the bottoms folded up. The bullion and metals going to make up the check are transferred to these directly from the scale pans after which they are folded over and made into compact bundles.

The cupels are placed in a row across the muffle and when they are hot the buttons are dropped quickly into them with the check in the middle. They should be cupelled at a low temperature so that plentiful crystals of litharge are obtained all around the buttons, but toward the end the temperature should be increased to insure driving off the last of the lead.

The buttons are cleaned, weighed, parted and the gold weighed. The per cent loss of gold and silver is determined and a corresponding correction made to the weights of gold and silver found. From these figures the fineness in both gold and silver is determined. The gold should check within 0.1 part and the silver within 0.5 parts.

Notes. 1. When the doré contains antimony weigh the samples into 2.5″ scorifiers with 30 grams of test lead. The proofs are made up according to the preliminary assay. All are scorified in the same muffle at the same time. Pour and hammer the lead buttons into a cube. Should the weight of these lead buttons vary over a gram, make up to the same weight with sheet-test-lead, cupel and part as usual.

2. When the doré contains bismuth, selenium or tellurium, three ½ gram

portions are weighed out into 2½″ scorifiers with forty grams of test lead, scorified and the lead buttons flattened out into a sheet about 3 inches square. This sheet of lead is dissolved in about 200 c.c., of dil. HNO_3 (1–3) and boiled to expel all red fumes. Dilute to 400 c.c., filter through triple folded 15 cm. filter, washing the precipitate only once. To the filtrate is added sufficient NaCl solution to precipitate all the silver. Heat to boiling and allow to stand over night. Filter through 15 cm. filter washing the precipitate only once. Place the two filter papers in a 2½″ lead lined scorifier, dry in an oven, burn, then cover with 30 grams of test lead and scorify. Open the scorification at a rather high heat, continuing with a gradually falling temperature. When the scorifiers have entirely closed over, close the muffle door, raise the heat and pour; then treat exactly as in No. 1.

If the silver fineness of the doré is not three or more times greater than the gold fineness, another set of assays must be run with the addition of proof silver at the weighing out of the doré.

U. S. Mint Assay of Gold Bullion.

Melting. Every lot of bullion or dust received at any U. S. Assay Office or Mint is immediately weighed and given a number. It is then sent to the melting room. Here it is melted in a graphite crucible with borax and soda and cast into a bar. Usually no attempt is made to refine it unless it is very impure. Occasionally, in the case of very impure bullions, a small dip sample is taken and granulated, but in general the whole melt is cast and sampled as noted below. The slag is poured with the bar and when solid is ground, panned and the recovered prills are dried, weighed and allowed for in computing the value of the bar.

Sampling. After the bar is cleaned of slag it is dried, weighed and numbered and from diagonally opposite corners two samples of 3 or 4 grams each are chipped. These are flattened with a heavy hammer, annealed and rolled into sheets thin enough to be easily cut with shears. The use of the shears can only be learned by practice, but assayers become very skillful after a time so that it is no unusual thing to see a bullion assayer weigh out five samples in almost as many minutes.

Preliminary Assay. Assay for Bases. To determine the approximate composition of the bullion a preliminary assay is made. A sample of 1000 gold weights (500 mgs.) is weighed out, wrapped in five grams of lead foil and cupelled. The weight of the bullion taken, less the weight of the button obtained gives the base metals.

The button now consists of gold and silver, the approximate relative proportions of which must be determined. This may be done by adding silver, cupelling and parting or by touchstone. This later method is used at the Government Assay Offices and Mints. The touchstone consists of a piece of black jasper on which the sample is rubbed and the mark compared with marks made with alloy slips (needles) of known compositoin. The needles range from 500 to

1000 fine and are 20 points apart. This gives the fineness within 2 per cent which is close enough to show how much silver to add to inquart the main assay and to make up the check or proof center.

Final Assay. The final assay is usually made by two assayers each working on one of the chipped samples. In the case of a small bar each makes one assay, while in the case of a large bar each assayer makes two or more assays. The balances used for the assay are usually adjusted so that a deviation of the needle of one division on the ivory scale amounts to some simple fraction of the weights used. Thus at one assay office a deviation of the swing of one division on the ivory scale amounts to 0.1 mg. = 0.2 gold weights. With this adjustment it is not necessary to make so many trials with the rider to get the final weight, nor is it necessary to weigh out exactly an even half gram of bullion for the assay. Instead we weigh out 1000 ± 3 divisions on the ivory scale, record the difference, and make a corresponding correction when the gold cornet is weighed.

As stated above the weight of bullion taken for each assay is 1000 (500 mg.). To this is added sufficient silver to make the ratio of silver to gold 2 to 1, and the whole is wrapped up in 5 or 6 grams of lead foil. The lead foil pieces are all cut to exact size, about $1\frac{1}{2}'' \times 2\frac{1}{2}''$, and rolled up into cornucopia shape with the bottom pinched in. The bullion is poured directly into these from the scale pan. The silver is added in the form of discs made for convenience into 4 or 5 different sizes. These discs are punched out of sheets carefully rolled to gauge so that the punchings will weigh exactly even tens and hundreds in the gold weight system. If the bullion contains no copper it is advisable to add about 30 parts gold weight (15 mg.). This copper may be alloyed with the silver used for parting.

One or more proofs of pure gold weighing usually 900 (0.450 grams) are also weighed and made up to the 2 to 1 ratio and copper added to approximate that in the bullion. These are wrapped in the same quantity of lead foil as the bullion, and one or more are run in each row of cupels in the muffle. The lead packets are pressed into spherical shape by pliers specially designed for the purpose.

The lead packets are put in order as prepared in the numbered compartments of a wooden tray and taken to the furnace room where they are cupelled in a rather hot muffle. The cupels are surrounded by a row of extra cupels so that the temperature may be kept as uniform as possible for all the assays. The cupels are withdrawn while the buttons are still fluid. With a two to one ratio of silver to gold, and with copper present, there is no danger of sprouting.

The buttons are removed from the cupels by means of pliers and carefully cleaned from all adhering bone-ash. They are then placed on a special anvil and flattened by a middle and two end blows with a heavy polished hammer. They are then annealed at a redheat and passed twice through the rolls which are adjusted each time so that after the second passage they are about 2½″ long by ½″ wide, and about as thick as an ordinary visiting card. It is important that the fillets be all of the same size and thickness with smooth edges. They are then re-annealed and each one is numbered on one end with small steel dies to correspond with the number of the assay, and rolled up into "cornets" or spirals between the finger and thumb, with the number outside. It is important that an even space be left between all turns of the spiral in order that the acid shall have easy access to all parts of the gold.

The cornets are parted in platinum thimbles which are supported in a platinum basket, and the whole thing is placed in a platinum vessel containing boiling nitric acid of 32° B. (Sp. Gr. 1.28). They are boiled for 10 minutes and then transferred to another vessel containing acid of the same strength and boiled 10 minutes longer. The basket and contents is then washed by dipping vertically in and out in three changes of distilled water, drained, dried, and annealed usually in the muffle.

When cold the cornets are ready to weigh. The gold should be entirely in one piece, and the original numbers easily discernable on the parted cornets. The proofs are weighed first and the corrections applied to other cornets. The proofs always show a slight gain in weight. The correction thus determined is termed the "surcharge," and is really the algebraic sum of all the gains and losses.

When more than 14 cornets are parted at one time the lot is given a preliminary 3 minute treatment in an extra lot of acid followed by the two regular 10 minute boilings.

The purpose of the copper which is added to the assays is to render the button tough and permit of its being rolled out into a smooth edged fillet. Without the copper, the fillet is apt to crack in rolling, or to come through with a ragged edge which might give rise to a loss in parting. The action of copper in this case is probably due to its effect in aiding in the removal of the last of the lead in cupelling.[1] The time required for cupellation is approximately 12 minutes.

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[1] Rose Trans. Inst. Min. & Met. 14 pp. 545.

CHAPTER XI.

THE ASSAY OF SOLUTIONS.

A large variety of methods for the assay of gold and silver bearing solutions have been published in the technical press, and quite a number of these have been adopted by assayers. These methods may be classified as follows:—

1. Methods involving evaporation in lead trays with subsequent cupellation, or scorification and cupellation of the tray and contents.
2. Methods involving evaporation with litharge and other fluxes followed by a crucible fusion and cupellation.
3. Methods in which the precious metals are precipitated and either cupelled directly or first fused or scorified and cupelled.
4. Electrolytic methods in which the precious metals are deposited directly on cathodes of lead foil, which are later wrapped up with the deposit and cupelled.
5. Colorimetric methods (for gold only) all of which depend upon obtaining the "purple of Cassius" color which may be compared with proper standards.

Evaporation in Lead Tray. This method is a good one on rich, neutral solutions containing only salts of the precious metals. A tray of suitable size is made by turning up the edges of a piece of lead foil. If many of these assays are to be made it is well to have a wooden block as a form on which the trays may be shaped. A tray $2'' \times 2'' \times \frac{3}{4}''$ deep is about right to hold 1 assay-ton of solution.

Having made a tray which will not leak, the solution is added and carefully evaporated to prevent spattering. The tray is then folded into a compact mass and dropped into a hot cupel.

Among the disadvantages of the method are the following: It does not permit of the use of a large quantity of solution, and therefore is suited only to rich solutions. If the solutions are acid they will corrode the tray, and if they contain salts other than those of gold and silver these will interfere with cupellation. As both $AuCl_3$ and $KAu(CN)_2$ are volatile at moderate temperatures, many assayers do not consider the method a reliable one for solutions of these salts.

Evaporation with Litharge. (First Method.) A measured quantity of the solution is placed in a porcelain evaporating dish and from 30 to 60 grams of litharge is sprinkled over the surface. The mixture is allowed to evaporate at a gentle heat to prevent both spitting and baking of the residue. When dry the residue is scraped out, mixed with suitable fluxes, transferred to a crucible and fused in the ordinary manner. The last portions remaining on the dish may be removed by means of a small piece of filter paper slightly moistened which is afterwards added to the charge.

Some assayers add a little fine silica and charcoal with the litharge. The soluble constituents of a crucible charge, soda and borax, should not be added to the solution as they form a hard cake which is difficult to remove from the dish. The most important point in the process is the proper manipulation of the temperature. If this is right there will be no spattering and the dry residue will come away practically clean from the dish after prying it up with the point of a spatula.

Evaporation with Litharge. (Second Method.) A measured amount of solution is evaporated in a porcelain or enameled iron dish to a small volume, so that when the litharge and silica of a crucible charge are added, they will absorb practically all of the liquid forming a thick paste. The heating is continued and the material is stirred constantly to keep the residue granular, and to prevent it from sticking to the dish. When dry the residue is cleaned out with the aid of a spatula and a mixture of soda, borax and are argols placed with it in a crucible which is heated to quiet fusion, poured and treated in the usual way.

This method requires more manipulation than the first one, and the only advantage is in a possible hastening of the process.

If any residue sticks to the dish it may be removed by rubbing it with a little fine silica on a piece of filter paper, the whole being afterwards added to the charge.

A modification of the foregoing evaporation methods consists in evaporating to a small volume without the addition of any reagents, and then transferring the concentrated solution to a small dish of very thin glass (Hoffmeister's dish). The solution is evaporated to dryness either with or without litharge, and the dish and contents broken up directly into a crucible containing the usual fluxes. The assay is finished in the usual manner. The advantage of this method lies in the fact that there is no chance for loss of residue by not properly cleaning the dish, as the dish and all are fused.

The evaporation method while somewhat long, is the most reliable and accurate one known, and is the standard with which all other methods are compared. By arranging to allow the evaporation to run over night, the samples taken one night may be assayed and reported early next morning. The method is adapted to the treatment of any quantity of solution and of almost any character. If the solution contains much sulphuric acid, the litharge may be converted into lead sulphate which is unsuited either to act as a flux or to provide lead for a collecting agent. A fusion made on such a substance using a carbonaceous reducing agent, will give either no button at all, or a button of matte. The reaction between lead sulphate and carbon is as follows:

$$PbSO_4 + 2C = PbS + 2CO_2$$

If the solution is one of $AuCl_3$ a little charcoal should be added during the evaporation to insure the reduction and precipitation of the gold, as in this way we avoid the danger of loss gold by volatilization as the chloride. The gold being precipitated on the charcoal is in the best possible position to be alloyed with the lead which will be reduced by the carbon.

Precipitation by Zinc and Lead Acetate. The Chiddey Method. (For Cyanide Solutions.) This method which was first described by Alfred Chiddey[1] is suitable for both gold and silver and is used almost exclusively in this country for the assay of cyanide solutions. It works equally well on strong or weak, foul or pure solutions, and almost any quantity may be taken. Many changes of detail have been suggested and innumerable modifications of the original process are found described in the technical press. The following method has been found satisfactory:

Take from one to twenty assay-tons of solution in a beaker or evaporating dish and heat. Add 10 or 20 c.c. of a 10 per cent solution of lead acetate containing 40 c.c. of acetic acid per liter. Then add one or two grams of fine zinc shavings rolled lightly into a ball. The gold, silver and lead will immediately commence to precipitate on the zinc. At first the solution may become cloudy but will soon clear as more of the lead is precipitated. Heat, but not to boiling until the lead is well precipitated. This usually takes about twenty or twenty-five minutes. Then add slowly (about 5 c.c. at a time), 20 c.c. hydrochloric acid (1.12 sp. gr.), to dissolve the excess zinc. Continue heating until effervescence stops. It is often found that action ceases while there is still some undissolved zinc remaining. This is entirely covered and thus protected from the acid by the spongy lead. To be sure that all the zinc is dissolved feel of the sponge with a stirring rod and drop a little hydrochloric acid from a pipette directly on it.

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[1] E. & M. J. 75, p. 473, March 1903.

As soon as the zinc is dissolved decant off the solution and wash the sponge two or three times with tap water. Next, moisten the fingers and press the sponge, which should be all in one piece, into a compact mass. Dry by squeezing between pieces of soft filter paper or by placing on a piece of lead foil and rolling with a piece of large glass tubing. Finally roll into a ball with lead foil, puncture to allow for steam escape, add silver for parting, and place in a hot cupel.

As soon as the zinc is dissolved the assay should be removed from the heat, and the sponge removed. If this is not done the lead will start to dissolve and the sponge will soon break up. Washing by decantation and manipulation with the fingers may appear crude, but after a little practice the operator becomes so proficient that there is practically no chance of loosing any of the lead.

If any considerable amount of water is left the assay will split in the cupel. To avoid this danger some assayers dry the assays on the steam table before cupelling. Any zinc left will also probably cause spitting. Chiddey recommends placing a piece of dry pine wood in the mouth of the muffle immediately after changing the cupels, probably with the idea that this aids to prevent spitting when some zinc has been left undissolved. When working with small quantities of solutions it is best to add water occasionally to maintain a volume of at least 100–150 c.c. The secret of keeping the lead from breaking up is not to allow the solution to come to a boil at any stage of the procedure.

Zinc dust is used by many chemists in place of zinc shavings, a small amount being added on the end of a spatula. Many chemists agree that ½ gram is sufficient.

William H. Barton[1] suggests the addition of a small piece of aluminum foil dropped into the solution after the hydrochloric acid is added, to prevent the dissolving of the lead and the consequent breaking up of the sponge by the hydrochloric acid after the zinc is all dissolved.

T. P. Holt[2] recommends the substitution of a square of aluminum foil for the zinc. The lead sponge is removed from the aluminum with a rubber-tipped stirring rod. Care must be taken to use a sufficiently thick sheet of aluminum (1/16″ does well), to prevent small pieces becoming detached. These would remain with the lead sponge and might cause the cupels to spit.

Precipitation as Sulphide.[3] Acidify five or ten assay tons

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[1] Western Chemist and Metallurgist, 4 p. 67, Feb. 1908.

[2] Mining & Scientific Press, 100 p. 863, June 1910.

[3] Henry Watson, E. & M. J. 66 p. 753, Dec. 1898.

of solution with HCl and heat to boiling. While boiling add a solution containing two grams of lead acetate and pass in a current of hydrogen sulphide until all the lead is precipitated. Allow to cool somewhat still passing in H_2S, then filter and dry. Collect the gold and silver with lead either by a crucible fusion or scorification assay. The method is said to be quick, accurate and economical.

Precipitation by Cement Copper.[1] To 8 assay tons of the solution add a few cubic centimeters of sulphuric acid, and one gram of finely divided cement copper. Hear to boiling and boil 10 minutes. Filter through a strong 7 inch paper and place on the drained filter one-third of a crucible charge of mixed flux. Place the filter in a crucible containing another third of a charge of flux, and cover with the final third. Fuse and cupel as usual. The filter itself furnishes the reducing agent for the assay. If cement copper is not available, a solution of copper sulphate may be added together with a small piece of aluminum foil. Boil until all the copper is precipitated and add the remaining aluminum foil to the fusion. This modification takes more time than the first.

Precipitation by Silver Nitrate[2] (For Gold in Cyanide Solutions). Add an excess of silver nitrate solution which will cause the gold and silver to precipitate as an auric-argentic-cyanide. Allow the precipitate to settle, filter through a thin paper, and wash several times. Dry the filter and either scorify with test lead or fuse in a crucible with litharge and the regular fluxes. The method gives fairly good results in solutions not too low in gold. With solutions very low in gold the precipitation of the gold is not perfect.

Precipitation by a Copper Salt[3] (For Cyanide Solutions Only). Add to one liter of solution in a two liter flask 25 c.c. of a 10 per cent solution of copper sulphate, then add 5 to 7 c.c. of concentrated hydrochloric acid and lastly 10 to 20 c.c. of a 10 per cent solution of sodium sulphite. Shake vigorously for at least two minutes then filter, dry, and fuse the filter and precipitate in the usual way. With weak solutions it is best to bring up the strength by the addition of cyanide before adding the copper salt. The gold and silver are carried down by the precipitate of cuprous cyanide formed. Assays may be completed in three hours and the results are said to be good on both low and high grade solutions.

[1] Albert Arents, T. A. I. M. E. 34 p. 184.

[2] Andrew F. Cross, Jl. Chem. Met. and Min. Soc. of So. Af. 1 p. 28, and 3 p. 1.

[3] A. Whitby, Proc. Chem. Met. and Min. Soc. of So. Af. 3 p. 6.

The Electrolytic Assay of Cyanide Solutions. The following method is abstracted from the Journal of the Chemical, Metallurgical and Mining Society of South Africa [1] which describes the method and installation used at the Kleinfontein Group Central Administration Assay Offices.

Ten-assay-ton samples of the solution to be assayed are placed in No. 3 beakers, which are held in a frame, and electrolyzed using a current of 0.1 ampere. The anodes used consist of ordinary 5/16 inch arc lamp carbons which are held in position in the center of each beaker by suitable clamps. They are arranged so that they may be lifted out of the solution when no current is passing. The cathodes are made from strips of ordinary assay lead foil $2\frac{1}{2}'' \times 9''$ with the lower edge coarsely serrated to allow for circulation of the solution. To connect with the battery a $\frac{1}{4}''$ strip is all but severed from one end of the foil, and turned upward to make a terminal. The two ends of the lead are brought together and connected by folding the edges, making a cylinder about 3 inches in diameter.

The time required for the complete deposition of the gold is four hours, after which the carbons are removed, the lead cathodes disconnected and dried on a hot plate. When dry, they are folded into a compact mass and cupelled.

With weak solutions a small quantity of cyanide should be added in order to decrease the resistance and thus accelerate the deposition of the precious metals. The author reports no difficulty in obtaining a complete and adherent deposit of the gold, which separates as a bright yellow deposit.

This of course was the only metal worked for on the Rand, but there seems to be no reason why silver as well as gold can not be determined by this method.

The principal advantage of the method lies in the small amount of actual personal attention required. The method works as well for a 20 A. T. sample as for one of 10 A. T. The time required for the deposition of the gold is somewhat longer than for some of the precipitation methods and this appears to be the principal disadvantage of the process.

Colorimetric Methods. (For Gold only.) Several attempts have been made to adapt the "Purple of Cassius" test to the estimation of gold in chlorine and cyanide solutions. So far as the author is aware, none of the methods have been adopted as practical assay laboratory methods in this country. They were used for a time in

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[1] Vol. 12 p. 90. C. Crichton.

one or two South African plants, but have never come into great favor. The two most promising methods were described by Henry R. Cassel (E. & M. J. 76 p. 661) and James Moir (Proc. Chem. Met. and Min. Soc. of So. Af. 4 p. 298) and to those original articles the interested reader is referred.

CHAPTER XII.

THE LEAD ASSAY.

The fire assay for lead consists of a reducing fusion with iron, fluxes, and some carbonaceous reducing agent, and is conducted much as is the iron nail assay for gold and silver ores except of course no litharge or other lead bearing flux is added. The object of the fusion is to reduce and collect all of the lead in a button free from other elements.

Lead Ores. Lead ores are classified by metallurgists as oxidized or sulphide ores, also as pure or impure ores. The oxidized ores contain the lead principally in the form of carbonate, occasionally as sulphate and rarely as oxide or in combination with phosphorous, molybdenum, vanadium, chromium, etc. The corresponding lead minerals are cerussite, $PbCO_3$ (77.6% Pb), anglesite $PbSO_4$ (68.3% Pb), minium Pb_3O_4 (90.6% Pb), pyromorphite $Pb_5Cl\ (PO_4)_3$ (75.6% Pb), vanadinite $3Pb_3(VO_4)_2\ PbCl_2$ (72.4% Pb) and wulfenite $PbMoO_4$ (56.5% Pb). The most important sulphide lead minerals are galena PbS (86.6% Pb) jamesonite $Pb_2Sb_2S_5$ (50.8% Pb) and bournonite $PbCuSbS_3$ (42.5% Pb). The principal associated minerals are argentite, pyrite, chalcopyrite, sphalerite, stibnite, quartz, calcite and dolomite, as well as the oxidation compounds of the above sulphides. *Impure ores*, from the assayers point of view are those containing more or less arsenic, antimony, bismuth, copper, zinc, and other rarer metals which interfere with the lead assay.

Besides ores, the assayer may have brought to him various furnace products such as litharge, slag, matte, flue dust and cupel bottoms.

The fire assay for lead is not always as accurate as a carefully made wet determination but it is so simple, inexpensive and rapid that for a long time it served to govern the purchase and sale of all lead ores. Today it is still largely used by the smelters and others for the assay of pure ores, although for ores containing such base metal impurities as antimony, copper, zinc, etc. the wet method is usually preferred.

The results of the fire assay may be either lower or higher than the actual lead content, depending on the nature and quantity of the other minerals present in the ore. Pure ores give low results owing to losses of lead by volatilization and slagging. Both the sulphide and oxide of lead are volatile at moderate temperatures and for this reason great care must be taken to keep the temperature as low as possible consistent with a proper decomposition of the ore, and of the lead compounds which are formed during the fusion. On the other hand lead compounds, particularly the oxide, tend to pass into the slag which tendency is increased by the presence of zinc, and to some extent by arsenic and antimony. Impure ores containing arsenic, antimony, bismuth and copper, usually give high results as these metals are partly or wholly reduced and pass into the lead button.

Quantity of Ore and Reagents Used. The amount of ore used is generally 10 grams, occasionally 5 grams. With low grade ores 20, 25, or more grams may be used. The reagents used are the alakli carbonates, borax-glass, some reducing agent usually argols or flour, and occasionally sulphur. Iron in some form is always used. It may be in the form of nails or spikes, coiled wire, or the crucible itself may be of iron, and in this case will be used over and over again until worn out. A very satisfactory way of introducing iron is to use a rail or boat spike 2½ or 3 inches long, and about 0.5 inches through. In this assay it is customary to use a mixture of sodium and potassium carbonates as the mixture fuses at a lower temperature than either one alone. The alkali carbonates act as fluxes for the silica, and serve to give a basic slag which is necessary in this assay. Usually from two to three times as much alkaline carbonate as ore is taken. Borax-glass acts as a flux for the metallic oxides for limestone and the other alkaline earths. From one-half to twice as much borax-glass as ore is used. An excess of reducing agent is always used to insure keeping the necessary strongly reducing condition. Sulphur is only occasionally used and then when assaying an oxidized ore containing copper.

In the lead assay it is customary to use a mixed flux called a "lead flux." This may be bought already prepared or may be made up in the laboratory. Many different formulas are given among which are the following:

	1.	2.	3.
Sodium-bicarbonate	12 parts	4 parts	6.5 parts.
Potassium carbonate	15 "	4 "	5.0 "
Borax-glass	7 "	–	2.5 "
Borax powdered	–	2 "	–
Flour	2 "	1 "	2.5 "

No. 1 and 2 are found in use in the Coeur d'Alene lead district where the fire assay for lead has been brought to the highest degree of perfection. No. 1 is better for ores having a basic gangue, No. 2 for siliceous ores. No. 3 is perhaps the best of all for general use.

About 30 grams of flux are intimately mixed with 10 grams of ore, a nail is inserted and a cover of 8 or 10 grams more of flux is added. Very few assayers use a cover of salt in the lead assay on account of the danger of the loss of lead as chloride.

The fusion should always be made in a muffle furnace owing to the better control of temperature available. In fact the secret of the successful fire assay for lead is largely in the proper manipulation and control of the temperature throughout the process.

At the start the temperature should be low, sufficient only to barely melt the charge. This is necessary owing to the fact that in the early part of the assay the charge is in active motion and particles of the various lead compounds are continually being brought to the surface, where if the temperature were high they would suffer an appreciable loss by volatilization. When the charge has finished boiling and most of the lead is reduced and collected in the bottom of the crucible there is less danger of a loss by volatilization, owing first to the fact that lead itself is not so readily volatile as are some of its compounds and second to the difficulty of migration of the molecules through the heavy layer of reducing slag which covers the lead.

After the boiling has entirely ceased the temperature is raised gradually to decompose the lead compounds which still remain in the slag. These are principally the silicate and the double sulphide of lead and sodium or potassium and require a bright yellow heat for their complete decomposition. The fusion period is finished when the nails can be removed free from shots of lead. Sulphide ores require a much longer fusion than oxides owing to the fact that their decomposition is effected principally by iron, and therefore time must be allowed for every particle of the charge to come into contact with the iron. Oxide ores, on the other hand, are decomposed by the carbon of the charge and as this is uniformly distributed a much shorter time will suffice. Sulphide ores will require from one to one and one half hours of fusion, oxide ores from three quarters of an hour to an hour.

Influence of Other Metals on Lead Assay. *Silver.* Practically all of the silver in an ore is reduced and passes into the lead button. If present in sufficiently large quantities a correction for it may be made, i.e., 291.66 oz. per ton equals one per cent.

Gold. This metal is also reduced and passes into the lead button, but it is usually present in such small quantities that it may be disregarded.

Arsenic. Arsenic is occasionally found in lead ores usually in the form of arsenical iron pyrite. During the assay part of the arsenic is volatilized as metal or as arsenic sulphide but the larger part remains in the crucible. Here it usually enters into combination with the iron forming a speiss. After pouring it will be found as a hard white button on top of the lead from which it may be removed by hammering. Little if any arsenic enters the lead button. Under certain conditions, i.e., a long fusion at a low temperature with high soda excess, the formation of a speiss may be prevented.

Antimony. This metal is frequently found associated with lead, usually however only in small amounts. In the assay with iron, antimony is reduced and passes into the lead button. Buttons containing antimony are harder and whiter than those from pure lead ores and when they contain much antimony are brittle, breaking with a bright crystalline fracture.

If much antimony is present (over one-half as much as the lead) an antimony speiss will be found lying on top of the button.

Bismuth. This metal is rarely found associated with lead ores, but if present will be reduced and pass into the lead buttons.

Copper. Copper is often found in lead ores in the form of chalcopyrite, chalcocite, and oxidized copper compounds. If the ore is fully oxidized and a high temperature is employed most of the copper will pass into the lead button. If the ore contains much pyrite or sulphur in other forms most of the copper will remain as a sulphide and be dissolved in the alkaline slag. A button containing copper will be hard and tough and may show a reddish tinge.

Iron. This metal is often present in lead ores usually in the form of iron pyrite. It goes into the slag forming either a silicate or a double sulphide of iron with sodium or potassium. The lead button is practically free from iron.

Zinc. Zinc is often found associated with lead in ores usually in the form of the sulphide. During the assay part of the zinc is volatilized and part remains in the slag. Zinc sulphide is only decomposed by iron at a very high temperature so that only a very small amount of zinc passes into the lead button. Zinc sulphide is practically infusible, so that if present in too great an amount, may make the slag thick and pasty, and thus interfere with the separation of the lead.

Procedure. Assay ores in duplicate using 10 grams of ore and 40 grams of prepared lead flux. Use a 12 or 15 gram muffle crucible. Weigh out first 30 grams of lead flux, place the ore on top of this and mix thoroughly with the spatula. Insert a spike or nails point downward and finally cover with 10 grams more of lead flux. Have the muffle only moderately red so that it will take at least 30 minutes from the time the charges are put in until they are boiled down. Close the door to the muffle as soon as the crucibles are in and after the charges are melted place two crucibles part full of soft coal in the mouth of the muffle just inside of the door, which should be kept as tightly closed as possible. Raise the temperature gradually to a bright yellow and continue at this temperature until the nails can be removed free from lead.

Finally take the crucibles from the muffle using a pair of muffle crucible tongs and without setting them down quickly remove the nails with a large pair of steel forceps, tapping against the side of the crucible and washing the nails in the slag to remove all adhering lead globules. Pour the fusion into a mold and when cool separate the lead from the slag and hammer clean. Weigh to centigrams and report the results in percentage. Duplicates should be checked within 0.5 per cent.

The slag should be black and glassy. If dull, more borax-glass should be added. It should pour well from the crucible and immediately after pouring, the crucible should be examined for shots of lead. If these are found it is usually an indication of too low a temperature at pouring.

Notes. 1. If the ore is an oxide and contains copper add a gram or two of finely pulverized sulphur to the charge to prevent the copper from entering the button.

2. The soft coal is added to insure reducing conditions in the muffle and it may be renewed if necessary. When a muffle is used solely for fusion purposes the hole in the back is stopped up, thus preventing the entrance of so much air.

3. The removal of nails and pouring must be done without a moments delay as the charges are small and cool rapidly.

4. If the ore contains much silver the button should be cupelled and the weight of silver found deducted.

5. The lead should be soft and malleable and a fresh cut surface should have the bluish gray color of pure lead. The button should be capable of being hammered out into a thin sheet without breaking or cracking. A button that is bright, brittle and brilliantly white in the fracture indicates the presence of arsenic or antimony.

6. If there is doubt regarding the purity of the lead button it may be tested by cupellation. The only metals except lead likely to be present are gold, silver, antimony, copper and possibly zinc; each of which gives characteristic indications in cupelling.

7. Crucibles may be used a number of times as they are but little corroded but those used previously for gold and silver assays *must not* be used for this assay as the slag left in them contains lead. It is well to use a special size of crucible for the lead assay in order to prevent errors from mixing crucibles.

Assay of Slags, Furnace Products and Low Grade Ores or Tailings. In the assay of low grade materials such as slags and tailings a larger quantity of ore should be used and a different mixture of fluxes. The slag should be between a singulo and a sub-silicate and part of the iron may be added in the form of filings. On account of the size of the charge it is well to add a number of nails, as this will lessen the time necessary for complete reduction.

The following charges have been found satisfactory:

Limestone (½–2% Pb)			Slag			Slag		
Ore	25	gm.	Slag	25	gm.	Slag	100	gm.
Na_2CO_3	25	“	Na_2CO_3	25	“	Na_2CO_3	50	“
K_2CO_3	20	“	K_2CO_3	20	“	K_2CO_3	–	
Borax-glass	20	“	Borax-glass	10	“	Borax-glass	10	“
Flour	10	“	Flour	10	“	Flour	10	“
Nails (20 penny)	5	“	Nails (20 penny)	5	“	Nails (20 penny)	5	“
20 gram crucible			20 gram crucible			30 gram crucible		

Allow some time at a high temperature to allow opportunity for all of the slag to come in contact with the iron.

Corrected Lead Assay. To recover any lead which may have been left in the slag the following procedure is recommended. Save all the slag and remelt in the original crucible with the spikes or nails formerly used. If the first slag was quite glassy and viscous in pouring, add from 5 to 15 grams more sodium carbonate. Heat to redness and drop into each crucible a lump of about 5 grams of potassium cyanide. Close the door to the muffle and heat to a bright yellow and pour as soon as quiet. Add the weight of any small button found to the lead from the original fusion.

Chemical Reactions of the Lead Assay.

With an ore containing $PbCO_3$, $PbSO_4$, PbS, SiO_2 and $CaCO_3$ the following reactions may occur:—

$PbCO_3 = PbO + CO_2$ (Begins at 200° C.)

$2\ PbO + C = 2Pb + CO_2$ (Begins at 550° C.)

$PbO + SiO_2 = Pb\ SiO_3$ (Begins at 625° C.)

$PbSO_4 + 2C = PbS + 2CO_2$ (Begins at a dark red heat.)

$7\ PbS + 4K_2CO_3 = 4Pb + 3\ (K_2PbS_2) + K_2SO_4 + 4CO_2$ (Begins at a red heat.)

If carbon were not present some oxide and sulphate would probably remain to react as follows:—

$PbS + 2PbO = 3Pb + SO_2$ (Begins at 720° C.)

$PbS + PbSO_4 = 2\ Pb + 2SO_2$ (Begins at 670° C.)

$2PbSO_4 + SiO_2 = Pb_2\ SiO_4 + 2SO_2 + O_2$ (High heat.)

Toward the end as the heat is raised to a bright red and above, the reactions with iron become of importance, particularly the following:—

$PbS + Fe = Pb + FeS$

$PbSiO_3 + Fe = Pb + FeSiO_3$ (Requires a bright yellow heat for completion.)

$K_2PbS_2 + Fe = Pb + K_2FeS_2$ (Requires a bright yellow heat for completion.)

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